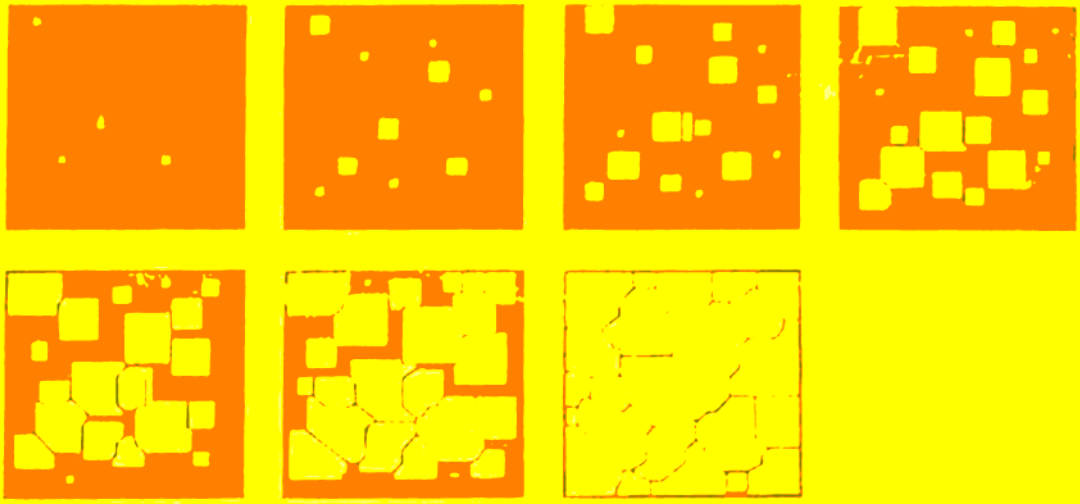

PHYSICAL METALLURGY

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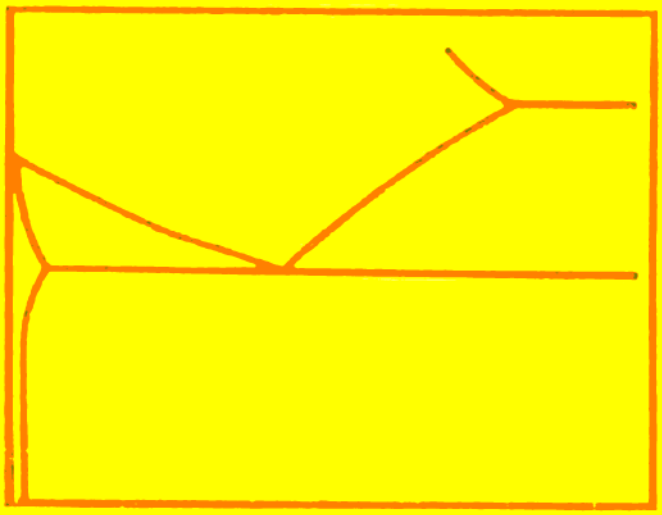

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PHYSICAL METALLURGY

A. GULYAEV

VOLUME 2

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PHYSICAL METALLURGY

А. П. ГУЛЯЕВ

МЕТАЛЛОВЕДЕНИЕ

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A. GULYAEV

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The Russian Alphabet and Transliteration

А а	a	К к	k	Х х	kh
Б б	b	Л л	l	Ц ц	ts
В в	v	М м	m	Ч ч	ch
Г г	g	Н н	n	Ш ш	sh
Д д	d	О о	o	Щ щ	shch
Е е	e	П п	p	ъ	”
Ё ё	e	Р р	r	ы	y
Ж ж	zh	С с	s	ь	’
З з	z	Т т	t	Э э	e
И и	i	У у	u	Ю ю	yu
Й й	y	Ф ф	f	Я я	ya

The Greek Alphabet

Α α	Alpha	Ι ι	Iota	Ρ ρ	Rho
Β β	Beta	Κ κ	Kappa	Σ σ	Sigma
Γ γ	Gamma	Λ λ	Lambda	Τ τ	Tau
Δ δ	Delta	Μ μ	Mu	Υ υ	Upsilon
Ε ε	Epsilon	Ν ν	Nu	Φ φ	Phi
Ζ ζ	Zeta	Ξ ξ	Xi	Χ χ	Chi
Η η	Eta	Ο ο	Omicron	Ψ ψ	Psi
Θ θ	Theta	Π π	Pi	Ω ω	Omega

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Part Four

ALLOY STEELS AND ALLOYS[1]

Chapter 14

EFFECT OF ALLOYING ELEMENTS

14.1. CLASSIFICATION OF IMPURITIES

To begin with, we should give definitions for alloy steel and alloying elements.

By the classification proposed by N. T. Gudtsov, all impurities (chemical elements) in steel may be divided into four groups:

1. **Permanent, or common, impurities.** This group includes manganese and silicon, and also aluminium. All these elements are used as deoxidants and are present in any well deoxidized steel (rimming steels are usually very low in silicon and aluminium), their addition to the metal is indispensable in steel manufacture. Sulphur and phosphorus should also be related to this group, since mass-produced steels cannot be fully freed from them. The content (percentages) of these elements in steels is usually as follows: 0.3-0.7 Mn, 0.2-0.4 Si, 0.01-0.02 Al, 0.01-0.05 P, and 0.01-0.04 S.

2. **Latent impurities.** These are oxygen, hydrogen and nitrogen, which are present in any steel in very low quantities. Methods of chemical analysis for these elements are very complicated, so that their content in steels is not given in common technical specifications.

3. **Occasional impurities.** This group includes impurities which can pass to steel from the charge materials or occasionally.

---

[1] By the system adopted in the book, iron alloys with more than 50 per cent iron are called steels and those with less than 50 per cent iron, simply alloys. This part of the book discusses alloy steels and alloys with a high (though less than 50 per cent) content of iron, as also alloys of nickel, titanium and other metals which have been classified as ferrous metals (Table 1.2).

For instance, the Urals iron ores contain a slight amount of copper which passes to the steel made from the ore. Steels smelted from the Kerch ores may be contaminated with arsenic. Remelting of tin-plated, zinc-plated or other steel scrap can bring tin, zinc, antimony, lead and other elements into the metal.

During the Second World War, carbon steels had an elevated content of chromium (0.1-0.3%) and nickel (0.2-0.3%) owing to a wide use of scrap of chromium and chrome-nickel steels.

4. **Alloying elements.** Elements which are intentionally added to steel in definite concentrations to obtain particular structure and properties of the metal are called *alloying elements.*

In that connection, steels containing alloying elements are called *alloy*, or *special*, *steels.*

Since the impurities of the three former groups are inevitably present in a steel owing to the specifics of steelmaking technology, they cannot be regarded, in these concentrations, as alloying elements, and the steel containing them cannot be regarded as an alloy steel.

For instance, a steel containing only 0.05-0.1 per cent vanadium (V) or 0.1 per cent titanium (Ti) is considered to be vanadium- or titanium-alloyed special steel, since these elements have been intentionally added to obtain special properties. If alloying elements are added in the amount up to 0.1 per cent, the process is called *microalloying.*

Common steels may contain up to 0.7 per cent Mn. If heavier alloying with manganese is needed, this element must be added to the steel in a correspondingly greater amount. Therefore, a steel containing, say, 1.0 per cent Mn is a manganese-alloyed steel and manganese in that concentration is an alloying element.

14.2. EFFECT OF ELEMENTS ON POLYMORPHISM OF IRON

All the elements which are soluble in iron can affect the temperature intervals of existence of allotropic iron modifications, i.e. can shift the points A_3 and A_4 along the temperature scale.

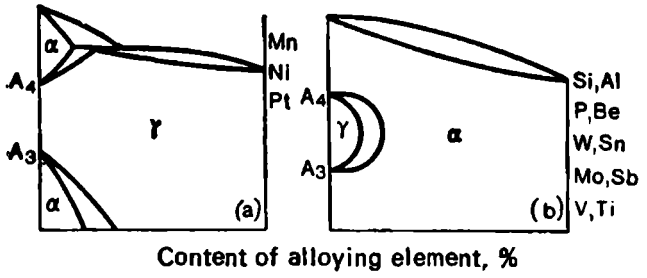


Fig. 14.1. Iron-alloying element constitutional diagrams (schematic)

Most of these elements either raise the A_4 point and lower A_3 point, i.e. widen the temperature range of the γ-modification, (Fig. 14.1*a*) or on the contrary, lower A_4 and raise A_3, i.e. narrow that range (Fig. 14.1*b*).

As may be seen from the schematic iron-alloying element constitutional diagrams in Fig. 14.1, with manganese, nickel or some other elements present in an amount above a definite concentration (Fig. 14.1*a*), the γ-state can exist stably from room temperature up to the melting point. Such iron-based alloys are called *austenitic*. With vanadium, molybdenum, silicon or some other elements present in an amount about a definite concentration, the α-state is stable in the whole temperature range (Fig. 14.1*b*). Such iron-based alloys are called *ferritic*. As distinct from other iron-based alloys, austenitic and ferritic alloys undergo no transformation on heating and cooling.

We analyse some real iron-alloying element constitutional diagrams.

Iron-nickel Systems (Fig. 14.2)[1]

Nickel has a face-centred cubic lattice of a parameter close to that of γ-Fe. Owing to this, γ-Fe and nickel can form a continuous series of solid solutions.

[1] This and the following diagrams (Figs. 14.2-14.6) are based on the critical analysis of numerous research studies of binary iron alloys and are given in a somewhat simplified form.

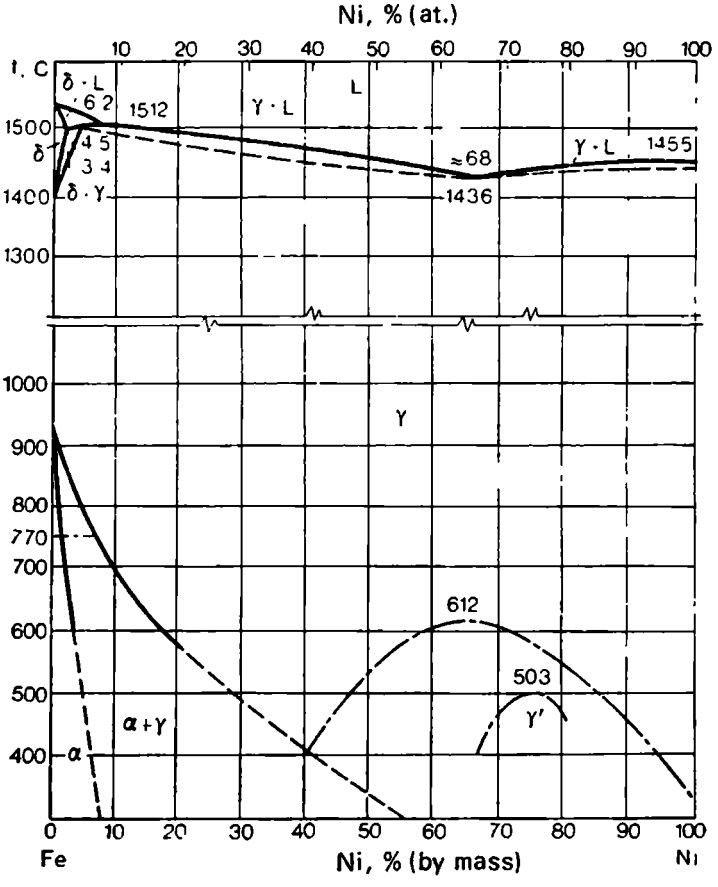


Fig. 14.2. Fe-Ni system

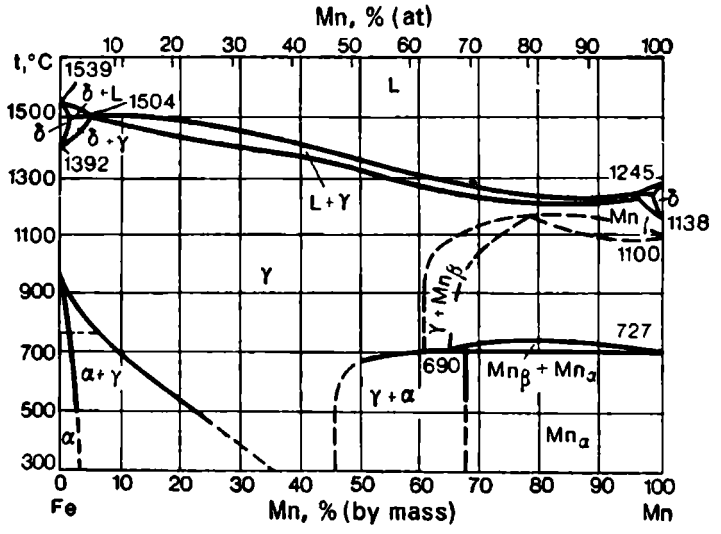
Nickel raises the A_4 point, so that a non-variant equilibrium $L + \delta \rightleftarrows \gamma$ takes place at 1 512°C, and lowers the A_3 point. The transformation temperatures of the system differ so markedly from those for pure iron that for practical use of the diagram it is advisable to indicate separately the temperature range of the transformation during cooling ($\gamma \rightarrow \alpha$ transformation) and during heating ($\alpha \rightarrow \gamma$ transformation). If, for instance, we take an alloy with 20% Ni at 300-400°C, it will have a practically stable γ-phase during heating and a stable α-phase during heating in the same temperature range. Since nickel sharply lowers the A_3 point, the transformation temperature of alloys with 10% Ni or more lowers down to 500°C or even greater. The diffusion of nickel in iron at such temperatures is hampered and the $\gamma \rightarrow \alpha$-transformation occurs by the martensitic (diffusionless) mechanism. At such concentrations of nickel, the reverse $\alpha \rightarrow \gamma$-transformation also takes place by diffusionless mechanism (see Fig. 10.39*a*).

In nickel-rich alloys, an ordered solid solution containing Ni_3Fe is likely to form. For an alloy with an exact proportion of Ni_3Fe (78% Ni), the ordering temperature (Kurnakov point) lies at 503°C.

Fe-Mn System (Fig. 14.3)

Manganese has four allotropic forms: α, which is stable at temperatures up to 727°C, β (727-1 100°C), γ (1 100-1 135°C), and δ (1 135-1 245°C). γ-Mn has a tetragonal face-centred lattice whose parameter is close to that of the face-centred lattice of γ-Fe. For that reason, γ-Fe and γ-Mn can form a continuous series of solid solutions. Disregarding the transformation in alloys very rich in manganese, whose specifics are due to the presence of the four allotropic modifications of manganese, the remaining portion of the Fe-Mn diagram is analogous to the Fe-Ni diagram.

Fe-Mn alloys are prone to undercooling, so that the γ-phase which, as may be seen in Fig. 14.3*a*, occupies a wide homogeneous region, is undercooled appreciably even at low cooling rates and undergoes a martensitic-type transformation.



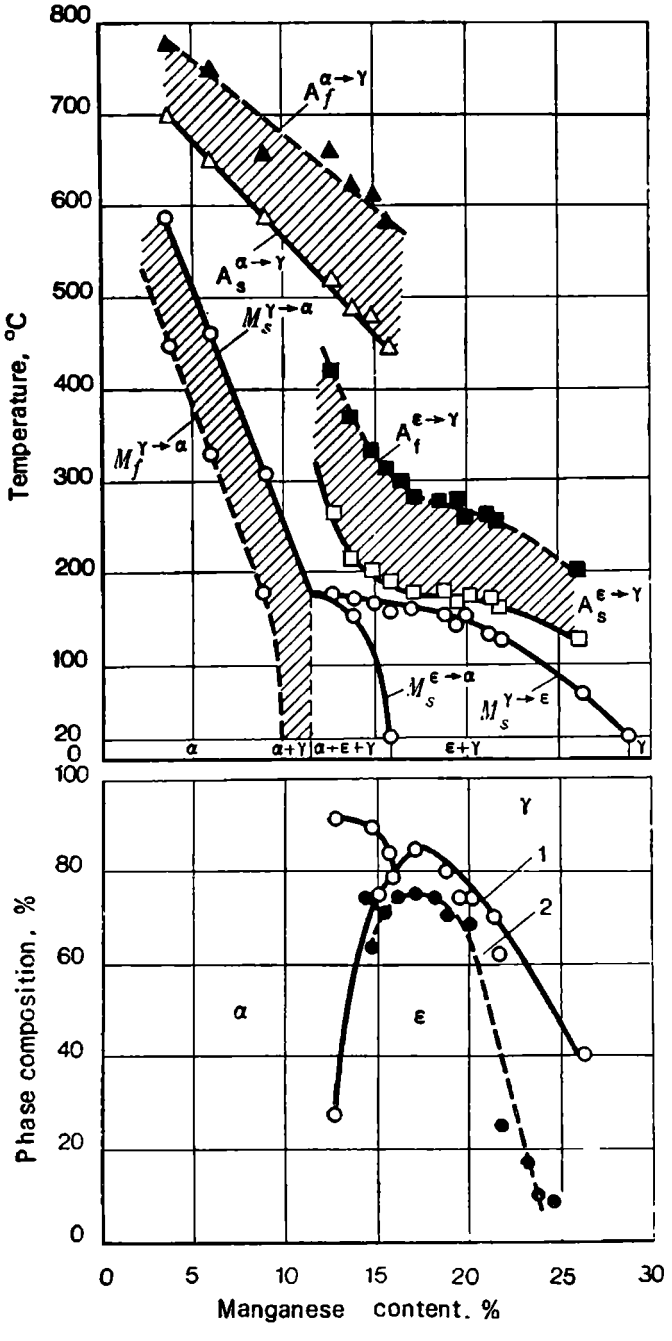
(a)

Fig. 14.3. Fe-Mn system (*a*) and the diagram (*b*) of direct and reverse martensitic transformations (light dots—the beginning and dark ones—the end of trans-

These martensitic phases are metastable and their formation is not indicated in the diagram of phase equilibria (Fig. 14.3*a*).

The temperature of metastable transformations in the Fe-Mn system is illustrated in Fig. 14.3*b*.

The complexity of phase transformations in this system consists in that three types of direct and reverse transformations are possible in it: (a) common $\gamma \rightarrow \alpha$ martensitic transformation which is realized at a manganese content up to 12 per



(*b*)

formation) and of phase states in Fe-Mn system (light dots — high-purity alloys, dark ones — common purity alloys)

cent; (*b*) $\gamma \rightarrow \varepsilon$ transformation with the formation of the hexagonal ε-solid solution, which is realized at 12-29% Mn and also occurs by the martensitic mechanism; and (c) $\varepsilon \rightarrow \alpha$ martensitic transformation which occurs in alloys with 12-17% Mn upon a partial $\gamma \rightarrow \alpha$ transformation.

It can be concluded therefore that ε is an intermediate phase in the $\gamma \rightarrow \varepsilon \rightarrow \alpha$ chain of martensitic reactions.

The lower portion of Fig. 14.3*b* is the phase diagram (showing the quantities of α, ε and γ phases at room temperature) for Fe-Mn alloys. Alloys with up to 12% Mn are single-phase (contain only the α-phase), those with 12 to 17% Mn are three-phase ($\varepsilon + \alpha + \gamma$), those with 17 to 29% Mn are two-phase ($\varepsilon + \gamma_1$), and those with more than 29% Mn are single-phase (γ-phase).

Heat treatment can only slightly change the proportion of these phases, but plastic deformation can increase the number of transformation phases (ε, α). The maximum concentration of the ε-phase that can be formed in alloys with 17% Mn without deformation is 80 per cent. With a heavy deformation, especially in uniform compression, the concentration of the ε-phase can be almost 100 per cent. Additions of cobalt and silicon increase the concentration of the ε-phase in high-manganese alloys. Owing to their specific properties, Fe-Mn alloys are promising for certain particular applications.

Fe-Cr System (Fig. 14.4)

Chromium has only one modification which crystallizes into a body-centred lattice isomorphous with α-Fe. Chromium lowers both points of allotropic transformations of iron, but the A_4 point is lowered more quickly, so that the two points finally merge together and the transformation region is closed at 13% Cr.

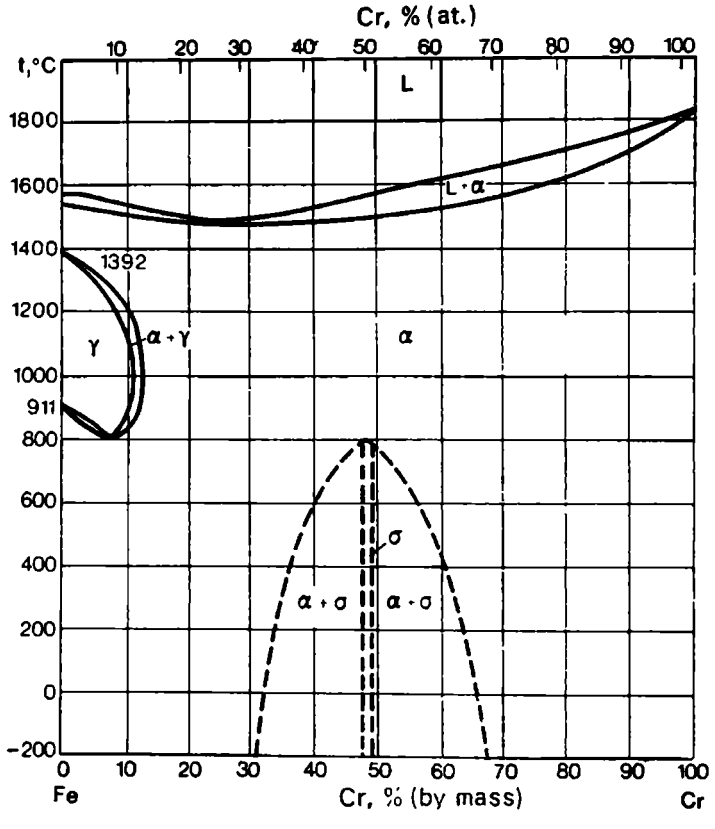


Fig. 14.4. Fe-Cr system

At the Cr : Fe ratio close to unity (at.%), there forms an unstable FeCr compound which is usually called the σ-phase. The upper temperature of existence of this compound is 815°C.

Iron-molybdenum System (Fig. 14.5)

Molybdenum has a body-centred cubic lattice, but its atomic radii differ from those of chromium and iron. That is why molybdenum cannot form a continuous series of solid solutions with α-Fe, as chromium does.

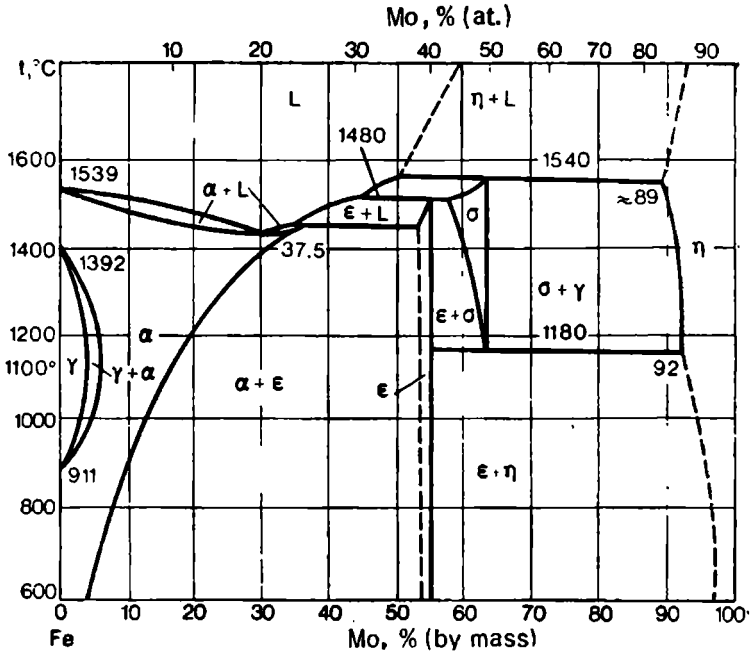


Fig. 14.5. Fe-Mo system

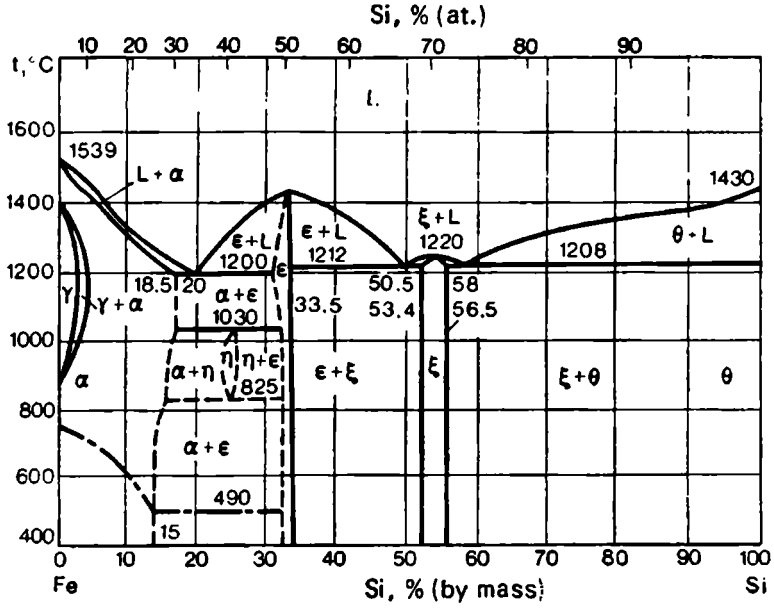


Fig. 14.6. Fe-Si system

The solubility of molybdenum in α-Fe at 20°C is 5 per cent and at 1 450°C it is at its maximum (26 per cent). Molybdenum raises the A_3 point and lowers the A_4 point and the transformation region wedges out completely at 3.5% Mo (2 at.%). All the metallic elements which raise the A_3 point and lower the A_4 point wedge out the γ-region at a content of approximately 2 at. per cent.

Iron-silicon System (Fig. 14.6)

Silicon has a diamond-like lattice. Its solubility in iron at 20°C is around 15 per cent. Silicon raises A_3 and lowers A_4 and thus wedges out the γ-region at 2% Si. Therefore, all alloys containing more than 2% Si (practically more than 2.5 per cent) are ferritic.

Silicon forms a number of compounds (silicides) with iron, which are denoted by Greek letters in the diagram (Fig. 14.6).

14.3. DISTRIBUTION OF ALLOYING ELEMENTS IN STEEL

In commercial alloy steels, which are multicomponent systems, alloying elements can be present: (a) in a free state; (b) as intermetallic compounds with iron or with one another; (c) as oxides, sulphides and other non-metallic inclusions; (d) in a carbide phase: as a solution in cementite or as individual carbon compounds—special carbides; (e) as a solution in iron.

We discuss in detail these possibilities.

1. Lead, silver and copper form no compounds with iron; besides, silver and lead are insoluble in solid iron, while the solubility of copper is roughly 1 per cent. That is why lead, silver or copper, if present in steel even in the slightest amount (copper in an excess of 1 per cent), will be in a free state as metallic inclusions. Steels alloyed with silver or with copper (in excess of 1 per cent) have no practical applications[1]. Therefore, cases when alloying elements are present in free state in steel are quite rare and deserve no detailed discussion.

2. Most of the alloying elements employed can form intermetallic compounds. This, however, is only possible at the concentrations of elements exceeding appreciably their usual concentrations in commercial steels. It can therefore be taken that intermetallic compounds of alloying elements are not present in common mass-produced steels.

In high-alloyed steels and special alloys, intermetallic compounds can play an important part.

3. Many elements having a greater affinity for oxygen than iron can form oxides and other non-metallic compounds. Such elements are added to the melt at the last stages of the steelmaking process; they take away oxygen from iron and thus deoxidize the steel: $FeO + M \rightarrow M_nO_m + Fe$.

[1] On lead-alloyed automatic steels see Sec. 7.7

In this general formula, *M* is an alloying element which serves as a deoxidant. The reaction results in the formation of Al_2O_3, TiO_2, V_2O_5 or other oxides[1].

Apart from having a greater affinity for oxygen, some elements may have a greater affinity for sulphur than iron. Upon being added to steel, these elements form sulphides.

The content of oxides, sulphides and other non-metallic inclusions in common commercial steels is not high and depends on the type of steelmaking process.

The highest content of non-metallic inclusions is found in rimming open-hearth steels and especially in Bessemer steels. Their content is lower in killed steel and still lower in electric steel. Steels produced by vacuum melting or electroslag remelting have the lowest content of non-metallic inclusions.

4. Many elements having a high affinity for carbon can be dissolved in cementite or can form individual carbide phases.

The formation of carbides in steel will be discussed later in this chapter. Here it suffices to note that only the elements which are to the left of iron in the Periodic Table can be considered as carbide-forming elements (Fig. 14.7).

Apart from their capability for forming carbides, these elements are soluble in iron. Therefore, they may be distributed in a certain proportion[2] between these two phases.

---

[1] Deoxidation with carbon has recently found a wide application. In that case the deoxidation products are gaseous ($2FeO + C = 2Fe + CO_2$) and can be fully removed from the metal by vacuum degassing.

[2] Mainly depending on the content of an alloying element and carbon.

I	1 H																2 He
II	3 Li	4 Be	5 B	6 C										7 N	8 O	9 F	10 Ne
III	11 Na	12 Mg	13 Al	14 Si										15 P	16 S	17 Cl	18 Ar
IV	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
V	37 Rd	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
VI	55 Cs	56 Ba	57-71 TR	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 Rn	86 At
VII	87 Fr	88 Ra	89-102 Ac															
	IA	IIA	IIIA	IVA	VA	VIA	VIIA		VIIIA		IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB

Fig. 14.7. Periodic Table. The elements in the frame can form carbides in steel

5. The majority of alloying elements (except for carbon, nitrogen, oxygen, boron and metalloids which are far from iron in the Periodic Table) can be dissolved in iron in appreciable quantities. The elements occupying places to the left of iron in the Periodic Table are distributed between iron (base) and carbides; those to the right of iron (cobalt, nickel, copper, etc.) can only form solutions with iron and do not form carbides.

Summing up, it may be stated that *alloying elements are predominantly dissolved in the main phases of iron-carbon alloys (ferrite, austenite, cementite) or form special carbides*[1].

14.4. EFFECT OF ALLOYING ELEMENTS ON FERRITE

The dissolution of alloying elements in α-Fe occurs owing to the substitution of iron atoms by the atoms of these elements. Since the alloying elements differ from iron in the size and structure of their atoms, the substitution atoms cause stresses in the iron lattice and thus change the lattice period. As has been shown in Fig. 4.6c, all the elements that are soluble in ferrite change the parameters of the ferrite lattice, the effect being greater at a larger difference between the atomic radii of iron and alloying element. The elements with an atomic radius smaller than that of iron diminish the lattice parameter and those with a greater atomic radius, increase it[2] (an exception is nickel). Naturally, a change in the size of α-lattice causes a change in the properties of ferrite: in particular, its strength may increase and plasticity, diminish.

Figure 14.8 shows how the properties (hardness, impact toughness)

[1] *Special carbides* are those formed by carbide-forming elements and whose formula and crystal lattice differ from the formula and lattice of cementite.

[2] Atomic radii of elements are given in Table 1.7.

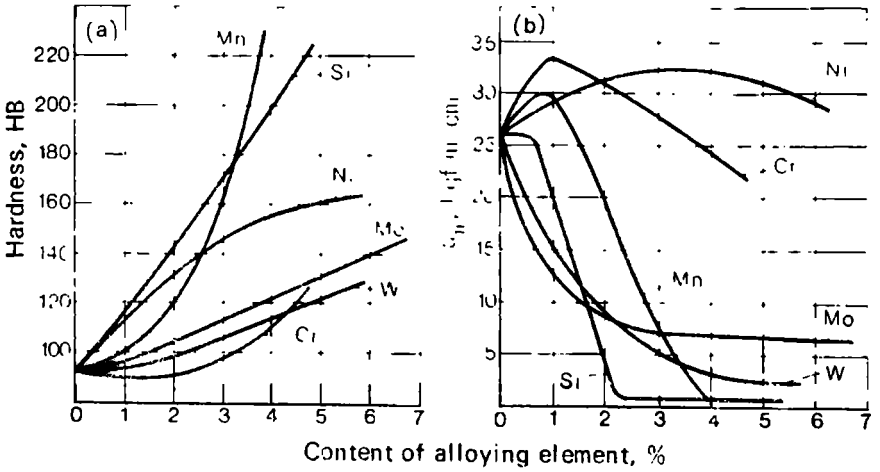


Fig. 14.8. Effect of alloying elements on the properties of ferrite (author's)
(a) hardness; (b) impact toughness

of ferrite change on dissolution of various elements in it. As may be seen from the curves, chromium, molybdenum and tungsten have a lower strengthening effect on ferrite than nickel, silicon or manganese. Molybdenum and tungsten, as also manganese and silicon (if these two elements are present in an amount of more than 1 per cent), lower the toughness of ferrite. Chromium diminishes the toughness of ferrite appreciably less strongly than do the elements mentioned, while nickel is ineffective in this respect.

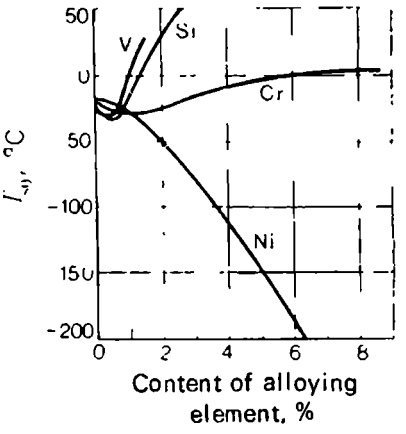


Fig. 14.9. Effect of alloying elements on ductile-to-brittle transition temperature (the author)

Of large importance is the effect of alloying elements on the ductile-to-brittle transition temperature which characterizes the liability of steel to brittle fracture. The presence of chromium in iron increases somewhat the ductile-to-brittle transition temperature, whereas nickel lowers this point appreciably and thus diminishes the liability of iron to brittle fracture (Fig. 14.9).

Thus, among the six alloying elements which are most common in steelmaking practice, nickel is the most valuable in its effect. It produces an appreciable strengthening effect on ferrite and lowers the ductile-to-brittle transition temperature, but does not lower the toughness of ferrite, whereas other elements either produce a weak strengthening effect on ferrite without lowering the toughness (such as chromium) or have a strong strengthening effect but sharply lower the toughness of ferrite (manganese and silicon[1]).

The curves shown in Fig. 14.8 have been obtained for slowly cooled alloys. The properties of ferrite containing silicon, molybdenum or tungsten in the solution practically do not depend on whether the alloy has been cooled quickly or slowly. On the other hand, if ferrite is alloyed with chromium, manganese or nickel, its hardness upon quick cooling turns out to be higher than that obtained on slow cooling. This circumstance is illustrated by the curves of Fig. 14.10.

A study of the causes of the strengthening of alloyed ferrite in practically carbonless alloys ($C < 0.02$ per cent) on quick cooling has shown that this is associated with the formation of a martensitic-type structure.

On slow cooling, there forms *polyhedral ferrite* (Fig. 14.11*a*). Quick cooling gives a structure of acicular type: *acicular ferrite* (Fig. 14.11*b*), which resembles bainite. The hardness of acicular ferrite is 100-150 Brinell numbers higher than that of polyhedral ferrite.

Why then the structure of acicular ferrite does not form in pure iron or in iron alloyed with tungsten, molybdenum or other elements?

[1] This effect of manganese and silicon is observed at Mn > 1-1.5 per cent and Si > 0.5 per cent.

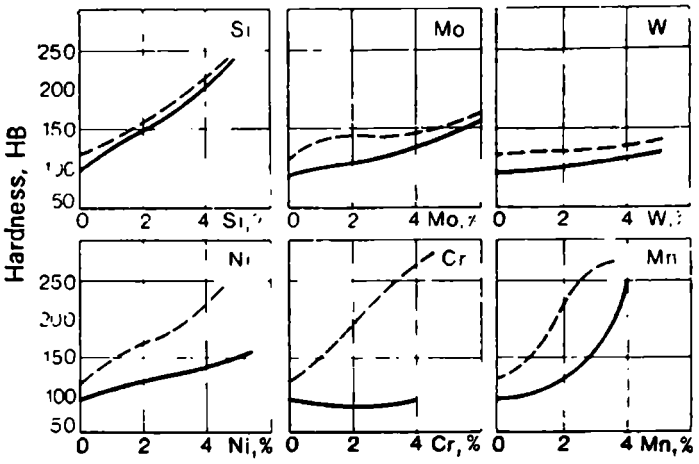


Fig. 14. 10 Effect of alloying elements on the hardness of ferrite (the author) dotted lines — as-hardened solid lines — as-annealed

In pure iron, it is impossible to obtain undercooling sufficient for suppressing diffusion movements of atoms to such an extent that the γ-modification would have no other possibility than to transform by the martensitic (shear) mechanism into acicular ferrite[1]. However, in the presence of an element which lowers the A_3 point (chromium, manganese or nickel) the required undercooling can be attained to form acicular ferrite.

The strengthening effect on the formation of acicular ferrite is due to what may be described as 'structural strain hardening': the $\gamma \rightarrow \alpha$-transformation is

[1] It is reported that a martensitic structure has been formed in coarse-grained specimens of pure iron by quick cooling.

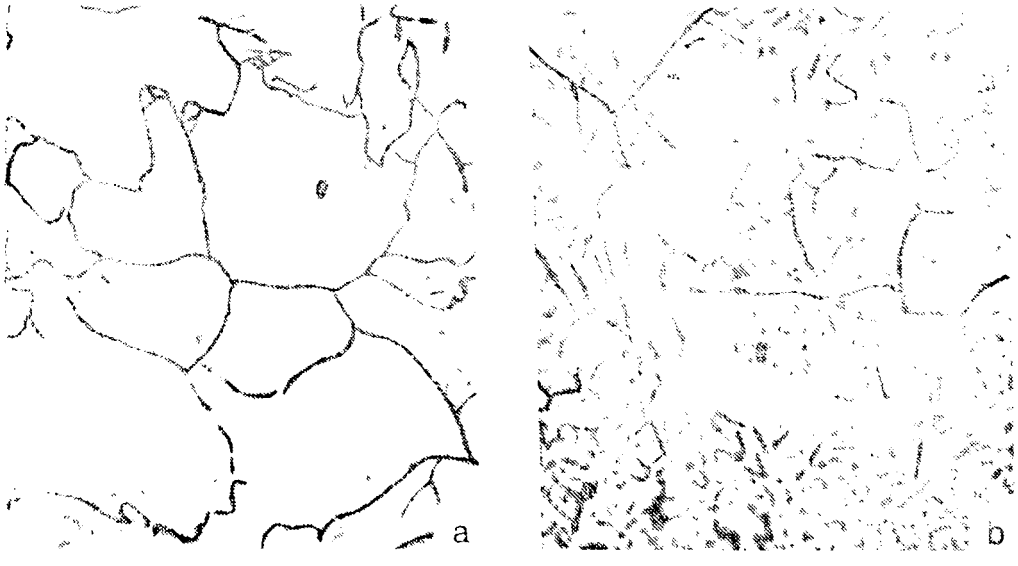


Fig. 14.11. The structure of ferrite in Fe + 4.2% Cr alloy
(*a*) polyhedral ferrite, slow cooling. ×400; (*b*) acicular ferrite, very quick cooling. ×400

accompanied with volume changes and since the transformation occurs at a reduced temperature (owing to undercooling), the γ- and α-phase undergo strain hardening. As a result of the transformation, the block structure of the alloy is comminuted appreciably on application of second-order stresses.

14.5. THE CARBIDE PHASE IN ALLOY STEELS

Carbides in steels can only be formed by the metals which occupy places to the left of iron in the Periodic Table (see Fig. 14.7). Like iron, these metals relate to transition-group elements, but have a less completed *d*-electron shell[1].

The farther to the left is an element position in the Periodic Table, the less completed is its *d*-electron shell.

There is enough evidence for assuming that, in the process of formation of carbides, carbon gives up its valence electrons to fill in the *d*-electron shell of an atom of metal, whereas the valence electrons acquired by the metal form a metallic bond which is responsible for the metallic properties of carbides.

Numerous experiments show that the elements located farther to the left in the Periodic Table, i.e. those having less completed *d*-electron shells, form more stable carbides. These circumstances enable us to formulate the general conditions for the formation of carbides in steels: *only the metals having a less completed d-electron shell than that of iron can be regarded as carbide-forming; the activity of a carbide-former is the greater and the stability of the carbide phases formed is the higher, the less completed is the d-electron shell of its atom*[2].

Using this rule. it is possible to formulate the conditions for the formation of carbides in steel in the presence of several carbide-forming elements, the sequence of dissolution of various carbides in austenite, and other factors which may be important for the theory of alloying, the practice of steelmaking, and the applications of alloy steels.

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[1] As is known from the course of physics, electrons form individual electron shells around atomic nuclei. Electrons on distant shells of an atom possess a higher level of energy. Each electron shell can be in turn divided into a number of energy bands which are designated by the letters *s*, *p*, *d*, and *f* (beginning from the nearest shell). Each band can contain a limited number of electrons. For instance, a *d*-band can contain not more than 10 electrons.

The number of electrons increases from hydrogen to other elements according to the atomic number of a given element, with electrons occupying first the shells of the least energy level, i.e. consecutively all the sites in the first shell, then in the second shell, and so on. In some elements, however, which are called transition-group elements, one or two electrons appear in the outermost (valence) shell before the *d*-band of the previous shell is completed. Among these elements are many metals, including iron and carbide-forming elements.

[2] This rule is a particular case of the conditions for the formation of carbides and nitrides in alloys. Any element whose *d*-electron shell is less completed than that of the main metal can serve as a carbide- or nitride-forming element in alloys of that metal.

In accordance with what has been said, carbides in steels can be formed by the following elements: titanium, vanadium, chromium, manganese, zirconium, niobium, molybdenum, hafnium, tantalum, and tungsten.

Nickel and cobalt carbides occur in the nature, but these metals cannot form carbides in steels, i.e. in iron-based alloys, since they contain more electrons in the *d*-shell than iron (7 in cobalt, 8 in nickel, and only 6 in iron). Thus, carbon gives up its electrons preferably to iron, and therefore no carbides of nickel or cobalt are formed.

The elements with a completely filled in *d*-electron shell (copper, zinc, silver, etc.) under no circumstances form carbides in alloys[1].

On the other hand, as follows from the above, the activity of carbide formation and the stability of carbides in alloy steels should increase from manganese and chromium to the elements having a less completed *d*-electron shell, such as molybdenum, vanadium, tungsten or titanium. This means, for instance, that if a steel contains both chromium and vanadium, it may be expected that vanadium carbides will form first (under equilibrium conditions).

Taking the atomic radius of carbon as 0.79 Å, it can be easily found that the ratio of the atomic radius of carbon to that of a metal is less than 0.59 for all carbide-forming elements except for iron, manganese and chromium.

As has been indicated earlier (Sec. 4.8), if the ratio of the atomic radius of a metalloid (carbon, nitrogen or hydrogen) to that of a transition-group metal is less than 0.59, these elements can form a special type of compounds called 'interstitial phases'.

For the majority of carbide forming elements, $r_c : r_m < 0.59$, and therefore, they can form interstitial phases with carbon.

As has been established, the following carbide compounds can form in steels:

Fe_3C Mn_3C $Cr_{23}C_6$, Cr_7C_3 Fe_3Mo_3C Fe_3W_3C	group-I carbides	Mo_2C W_2C, WC VC TiC NbC TaC, Ta_2C ZrC	group-II carbides (interstitial phases)

These carbides, however, cannot exist in pure form in steels. Carbides of all alloying elements contain iron in the solution and, in the presence of several carbide-forming elements, also these elements. In chrome-manganese steel, for instance, a complex carbide $(Cr, Mn, Fe)_{23}C_6$ (which contains iron and manganese in the solution) forms instead of the pure chrome carbide $Cr_{23}C_6$.

Carbides of a similar chemical formula are mutually soluble. Therefore, if for instance, a steel is simultaneously alloyed with titanium and niobium there will form a complex carbide of titanium

[1] In very rare cases, carbides of boron, aluminium, silicon and some other elements which by the adopted classification are regarded as non-carbide-forming, can form in metallic alloys. The point is that these carbides, such as B_4C, Al_3C_2, are utterly different from the carbides being considered. They are covalent-bond compounds possessing no metallic properties.

and niobium, rather than two separate carbides of these metals. For that reason, there are fewer probable variants of the formation of carbides than have been given earlier and actually only the following six types of carbide are found in steels:

M_3C, $M_{23}C_6$, M_7C_3, M_6C — group-I carbides; MC, M_2C — group-II carbides

where M is the sum of carbide-forming elements (metallic). The ratio between the metallic elements and carbon (for non-distorted lattice) is given by the formula.

The carbides related to the first group have a complicated crystal structure. A typical carbide of that group is cementite whose crystal structure has been shown in Fig. 6.6.

The specific feature of the carbides of the second group (interstitial phases) is that they have a simple crystal lattice and crystallize usually with a large deficiency in carbon.

It should be noted that interstitial phases are hardly soluble in austenite. This means that they cannot pass into the solid solution on heating (even at a very high temperature). In this respect they may be easily distinguished from group-I carbides which are easily dissolved in austenite on heating. All carbide phases have a high melting point and a high hardness. The interstitial phases excel in that respect the group-I carbides.

The sequence of dissolution of carbides in austenite is determined by their relative stability and the degree of passage to the solution, by their concentration[1]. For instance, if three carbides (M_7C_3, M_6C, and MC) are present in an alloy, the austenite will be first saturated with M_7C_3 carbide (for instance, Cr_7C_3), whereas M_6C and MC carbides (say, of tungsten and vanadium) may remain in an excess.

14.6. EFFECT OF ALLOYING ELEMENTS ON TRANSFORMATIONS IN STEEL

Effect of Alloying Elements on the Kinetics of Austenitic Breakdown

As has been given in Ch. 10, the kinetics of austenitic breakdown determines the behaviour of a steel in heat treatment. Alloying elements may have a very strong effect on the kinetics of austenitic transformation.

[1] Since γ-Fe has a limited capability for dissolving carbon.

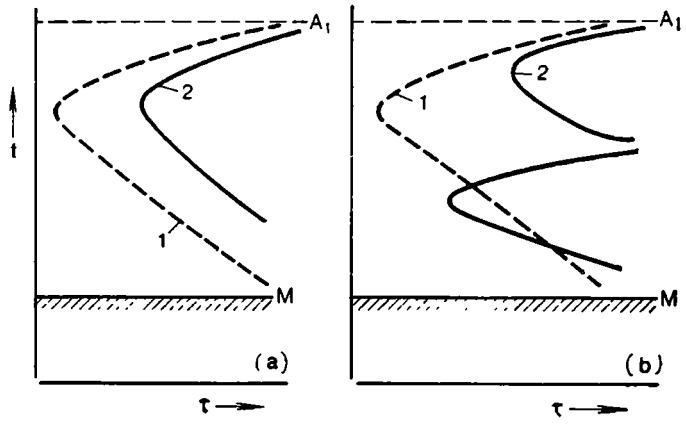

Fig. 14.12. Diagrams of isothermal decomposition of austenite

(*a*) carbon steel (*1*) and steel alloyed with non-carbide-forming elements (*2*); (*b*) carbon steel (*1*) and steel alloyed with carbide-forming elements (*2*)

The elements which are dissolved in ferrite or cementite without forming special carbides can have only a quantitative effect on the transformation processes. They can either accelerate the transformation (only cobalt acts in that way) or produce a decelerating effect (the majority of elements, including manganese, nickel, copper, etc.).

The carbide-forming elements may also cause qualitative changes in the kinetics of isothermal transformation. For instance, the alloying elements which form austenite-soluble carbides, have a different effect on the rate of austenitic breakdown at various temperatures: they slow down the transformation at 700-500°C (the formation of pearlite), slow it down quite appreciably at 500-400°C, and speed up the transformation at 400-300°C (the formation of bainite).

Thus, in steels alloyed with carbide-forming elements (chromium, molybdenum, tungsten) there are observed two maxima of the rate of isothermal decomposition of austenite, which are separated by a region of a high stability of undercooled austenite. The isothermal breakdown of austenite has two clear transformation ranges: the transformation into lamellar structures (pearlitic transformation) and the transformation into acicular structures (bainitic transformations).

The diagram of isothermal transformation is shown schematically in Fig. 14.12 (only the beginning of the transformation is shown).

Of the highest practical importance is the capacity of alloying elements to slow down the rate of austenitic breakdown in the range of pearlitic transformation, which is expressed in the shift of the curve to the right in the diagram of isothermal breakdown of austenite[1]. This favours a deeper hardenability and a greater undercooling

[1] The retarding effect of alloying elements on breakdown of undercooled austenite has been analysed in a number of fundamental studies (V.S. Sadov-

of the austenite to the interval of martensitic transformation on slower cooling, for instance, on cooling in oil or air, which is naturally associated with a reduction in the critical quenching rate.

As to the estimation of the relative effect of various elements on hardenability, the available data disagree quantitatively. The greatest effect on hardenability have chromium, nickel, molybdenum and manganese and these elements enter the composition of most structural alloy steels.

The hardenability of steel can be increased especially greatly by combined alloying with several elements. Such, for instance, is the combined effect of nickel and chromium.

Molybdenum is very effective when added to chrome-nickel steel.

Strong carbide-formers, such as vanadium, titanium, niobium and partially tungsten, have a peculiar effect on the kinetics of decomposition. Since these elements form hardly soluble carbides, they remain combined into carbides in the metal at common hardening temperatures (800-900°C) and do not pass to austenite. This results in a lower hardenability of steel, since the carbides act as crystallization centres for pearlite. At a high temperature of heating for hardening, these carbides are dissolved in the metal; the austenite contains these elements in the solution and therefore, the hardenability of the steel increases.

Experiments have shown that small additions of certain elements may be very effective in increasing the hardenability, but have no such effect when added to the steel in larger concentrations. Boron is first to be mentioned among such elements. A few thousandths of a per cent of this element can increase appreciably the hardenability, since all the boron passes to the solution, concentrates in thin boundary layers of austenitic grains and diminishes the rate of nucleation of pearlite[1].

The optimal content of boron to ensure the highest hardenability of steel is only 0.002-0.006 per cent; at a higher content of boron, its concentration at the boundaries of austenitic grains exceeds the saturation limit, resulting in the appearance of excess boric phases (borides) which act as crystallization centres for pearlite and diminish the hardenability of steel.

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sky, M.E. Blanter, R.I. Entin, R.F. Mehl, A. Hultgren, etc.). This effect may be explained by several factors, among which the main one is evidently that the diffusion of alloying elements is essential for the formation of carbide in the pearlitic transformation in alloyed steel, whereas only the diffusion of carbon is needed to form cementite (Fe_3C) in carbon steel.

Bainitic transformation involves no redistribution of alloying elements, with only carbon being redistributed, because of which the effect of alloying elements on the rate of bainitic transformation is not high (if this effect manifests itself, it acts in accelerating the transformation, though not always).

[1] As has been shown earlier (Sec. 10.3), pearlitic nuclei are mainly formed at the boundaries of austenitic grains.

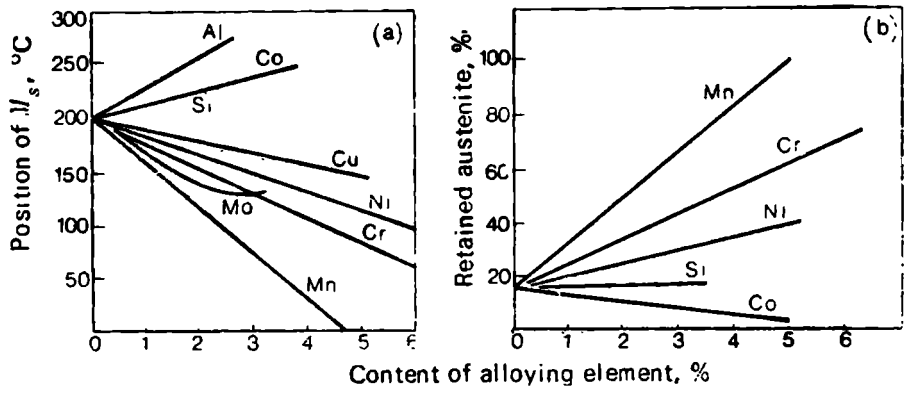

Fig. 14.13. Effect of alloying elements on the temperature of martensitic transformation (*a*) and the quantity of retained austenite (*b*). The steel contains 1% C (V. D. Sadovsky)

Effect of Alloying Elements on Martensitic Transformation

Alloying elements do not affect the kinetics of martensitic transformation, which is evidently similar in all types of steel. Here, their effect is exclusively on the position of the temperature range of martensitic transformation; this in turn affects the quantity of retained austenite that is fixed in hardened steel. Some elements (aluminium, cobalt) raise the point of martensitic transformation and reduce the quantity of retained austenite, other (silicon) have no effect, whereas most elements lower the martensitic point and increase the quantity of retained austenite (Fig. 14.13). As may be seen from the figure, 5 per cent of Mn lower the martensitic point down to 0°C, and therefore, at this (or a lower) content of this alloying element, the austenitic state can be fixed by cooling.

Effect of Alloying Elements on Coarsening of Austenitic Grains

All alloying elements inhibit coarsening of austenitic grains. Exceptions are manganese and boron which promote grain coarsening. Other elements which refine grains produce a different effect: nickel, cobalt, silicon, and copper (i.e. the elements that form no carbides) only weakly effect grain coarsening; chromium, molybdenum, tungsten, vanadium, and titanium refine the grain appreciably (they are mentioned in the order of increasing effect). This difference is a direct consequence of the different stability of the carbides (and nitrides) of these elements. Excess carbides, since they are not dissolved in austenite, inhibit grain coarsening (see the theory of bar-

riers, Sec. 10.2). That is why a steel containing even a slight quantity of undissolved carbides can retain a fine-grain structure up to very high temperatures of heating.

Effect of Alloying Elements on Transformations on Tempering

Alloying elements retard the process of martensite breakdown. Some of the elements, such as nickel or manganese, have only an insignificant effect, whereas the effect of most elements (chromium, molybdenum, silicon, etc.) is quite noticeable.

This is associated with the fact that the temper processes are diffusional in their nature and most of the alloying elements retard the carbide transformation, especially at the coagulation stage.

At the initial stage of martensitic breakdown in alloy steels, there forms ε-carbide whose composition (in alloying elements) is the same as that of martensite (this has been demonstrated by S. Z. Bokstein). At this stage of tempering, the effect of alloying elements on softening of austenite is not high. At a higher temperature there occurs a disruption of coherence with ε-carbide being transformed into cementite or a special carbide. Thus, softening takes place at this stage of tempering. Most of the alloying elements shift these processes upwards along the temperature scale.

To obtain similar results, steels alloyed with such elements as chromium, molybdenum, silicon, etc. must be heated in tempering to a higher temperature than that recommended for carbon steels or must be heated for a longer time.

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Chapter 15

CLASSIFICATION AND GRADING OF ALLOY STEELS

15.1. CLASSIFICATION OF ALLOY STEELS

Alloy steels can be classified by the four features as follows: the equilibrium structure, the structure upon air cooling, the composition, and the application.

Classification by Equilibrium Structure

1. *Hypoeutectoid steels* which contain excess ferrite in the structure;
2. *Eutectoid steels* whose structure is pearlite;
3. *Hypereutectoid steels* whose structure contains excess (secondary) carbides.
4. *Ledeburitic steels* whose structure contains primary carbides which have precipitated from molten steel[1]. In as-cast steel, excess carbides and austenite form a eutectic—ledeburite, which disintegrates on forging or rolling into separate carbides and austenite

[1] As regards their structure, ledeburitic steels should be related to (white) cast irons. Iron-carbon alloys with more than 2.0 per cent carbon (i.e. cast irons) are not malleable when contain ledeburite in the structure. In alloy steels, ledeburite forms at a lower content of carbon. The presence of ledeburite in alloy steels makes forging more difficult, but not impossible.

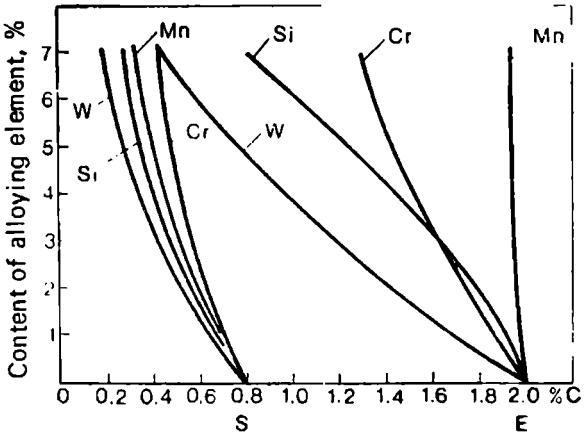

Fig. 15.1. Effect of alloying elements, on the position of *S* and *E* points

According to the Fe-C diagram, hypoeutectoid steels contain up to 0.8 per cent carbon, eutectoid steels roughly 0.8 per cent, hypereutectoid steels 0.8-2.0 per cent, and ledeburitic steels more than 2.0 per cent carbon.

Most alloying elements shift the points S and E (in the Fe-C constitutional diagram) towards a lower carbon content, because of which the boundary between hypoeutectoid and hypereutectoid steels and between hypereutectoid and ledeburitic steels for alloy steels passes at a lower carbon content than for carbon steels. For instance, with a chromium content of 5 per cent, a steel is hypereutectoid if it contains 0.6% C and ledeburitic, if it contains 1.5% C. The effect of various elements on the position of S and E points is shown in Fig. 15.1.

As has been noted, at a high concentration of an element which narrows the γ-region, there can be no $\gamma \rightleftarrows \alpha$-transformation (ferritic alloys). Consequently, the class of ferritic steels is obtained at a high concentration of an element which can narrow the γ-region and at a low content of carbon (which widens the γ-region).

The class of austenitic steels can be obtained in the same manner. At a sufficiently high content of an element which widens the γ-region, there are obtained steels in which austenite is retained on cooling up to the room temperature.

Therefore, in addition to hypoeutectoid, eutectoid, hypereutectoid and ledeburitic class of steels, there also may be alloy steels of ferritic and austenitic class[1].

Classification by the Structure Upon Air Cooling

Considering the structure formed upon the cooling of thin specimens in quiet air, all steels can be divided into three main classes[1]: (a) pearlitic, (b) martensitic, and (c) austenitic.

Pearlitic-class steels can be characterized by a low content in alloying elements, martensitic—by a more appreciable content, and austenitic—by a high content in alloying elements.

Let us see how the production of these steels may be associated with the kinetics of austenitic breakdown.

The production of these three classes of steel is based on the fact that the stability of austenite in pearlitic region increases as the content of alloying elements is increased and the temperature range of martensitic transformation is lowered; this is reflected in the diagrams of isothermal breakdown of austenite (Fig. 15.2).

With alloy steels of pearlitic class (as with carbon steels), the curve of the cooling rate in air intersects the region of pearlitic breakdown and gives the structure of pearlite, sorbite or troostite.

With martensitic steels, the region of pearlitic breakdown is already shifted appreciably to the right. For that reason, air cooling

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[1] Two intermediate classes—semiferritic and semiaustenitic steels—can also be singled out; these are steels in which the $\gamma \rightleftarrows \alpha$-transformation takes place only partially.

[2] This classification has been suggested by L. Guillet of France and is sometimes called Guillet's classification; the classification by the structure in equilibrium belongs to P. Oberhoffer and is often called after him.

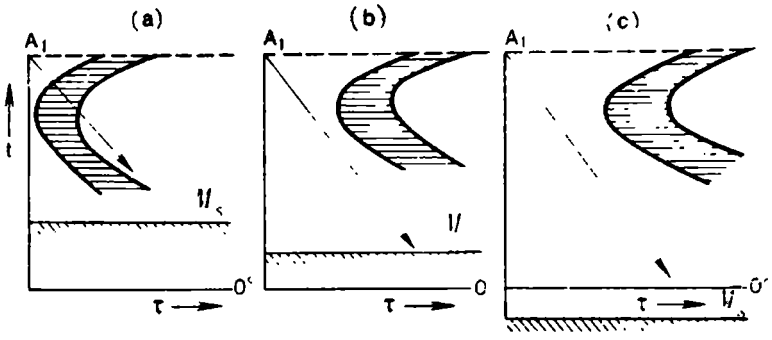

Fig. 15.2. Diagram of isothermal decomposition of austenite for three classes of steel (schematic)

(*a*) pearlitic class; (*b*) martensitic; (*c*) austenitic

causes no transformation in the pearlitic region, i.e. austenite is undercooled without breakdown to the temperature of martensitic transformation and the structure formed is martensite.

A further increase in the content of carbon and alloying elements not only shifts the region of pearlitic breakdown to the right, but also lowers the martensitic point to a sub-zero temperature. In that case the steel will retain the austenitic structure upon cooling in air to room temperature.

Note that the classification considered is conditional and relates to the air cooling of relatively thin specimens. Various steel structures can be obtained by varying the cooling conditions. For instance, a martensitic structure can be obtained by hardening of pearlitic steel or, on the other hand, a martensitic-class steel can be made pearlitic by slow cooling. Sub-zero cooling of austenitic steel can cause martensitic transformation in it.

Classification by Composition

Depending on their composition, alloy steels are classed into nickel steels, chromium steels, chrome-nickel, chrome-nickel-molybdenum steels and the like, i.e. are classified by the presence of various elements in them.

Classification by Application

According to application, all steels are divided into the main groups as follows.

Structural steels which are used to make machine parts. *Structural (machine-building)* steels are usually heat treated at the consumer. For that reason they are subdivided into cementable (i.e. suitable

for cementation) and improvable (to be subjected to hardening and tempering, not necessarily to high-temperature tempering).

A separate subgroup includes *constructional* steels which are mainly used in civil engineering. They are close in composition to structural steels, but are not heat treated at the consumer. Often they are also called *low-alloy* steels.

Tool steels are used to make various cutting and measuring instruments, forging and stamping dies, and the like. Tool steels are conditionally subdivided into *carbon*, *alloy*, *die* and *high-speed* steels.

Steels and alloys with special properties. This group includes steels possessing a particular special property, such as *stainless*, *heat-resisting* and *refractory*, *wear-resisting* steels, steels having a *particular pattern of thermal expansion*, steels with *special magnetic* or *electric properties*, etc.

In some cases steels of this group contain so much of alloying elements that they should be more properly classed with complex multicomponent alloys, rather than with steels (iron alloys). There is, however, no sharp boundary between such alloys and steels[1] and they should be considered together. Furthermore, some of such alloys may contain no iron at all, but in their properties and applications they are close to steels, i.e. alloys in which the base element is iron.

15.2. GRADING OF ALLOY STEELS

The designation (grading) of steels is specified by the USSR State Standards (GOST's) and includes a few letters and numerals indicating the approximate composition of a particular grade of steel.

Alloying elements are designated by Russian letters as follows: Н—nickel; Х—chromium; К—cobalt; М—molybdenum; Г-manganese; Д—copper; Р—boron; Б—niobium; Ц—zirconium; С—silicon; П—phosphorus; Ч—rare-earth metals; В—tungsten; Т—titanium; А—nitrogen; Ф—vanadium; and Ю—aluminium.

The first digits in a designation indicate the average content of carbon in hundredths of a per cent (or in tenths of a per cent for high-carbon tool steels). The digits following a letter indicate the approximate content of a particular alloying element (no digit is written if the content of an element is less than 1 per cent, a digit '1' is written if its content is roughly 1 per cent, '2', if the content is around 2 per cent, and so on).

Therefore, a steel containing 0.10-0.15% C and 1.3-1.7% Mn is graded as 12Г2; a steel with 0.28-0.35% C, 0.8-1.1% Cr, 0.9-1.2% Mn, and 0.8-1.2% Si, as 30ХГС, etc.

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[1] It is taken conditionally (USSR State Standard (GOST) 5632—72) that alloys containing in the total more than 50 per cent of alloying elements must not be called steels.

A letter '*A*'[1] at the end of a designation relates to high-quality steels which are made under more rigid technological requirements and are less contaminated with sulphur and phosphorus (S $<$ 0.03% and P $<$ 0.03%).

In some cases (especially with complex-alloyed steels), shorter designations are used. For instance, with tool steels containing more than 1% C the digits relating to the carbon content are omitted, so that a tool steel, say, with 1.45-1.70% C, 11.0-12.5% Cr and 0.5-0.8% Mo is designated as X12M.

Non-standard steels can be designated in various ways. For instance, experimental steel melts made at the Elektrostal' steelmaking works may be designated as ЭИ179, ЭИ276, ЭП398, etc., where the letter Э stands for Elektrostal', И—for research melts, П for experimental melts, and the digits are an ordinal number of a melt.

[1] Not to be confused with an 'A' standing in the middle of a designation and indicating that the steel has been alloyed with nitrogen.

Chapter 16

STRUCTURAL STEELS

16.1. MECHANICAL PROPERTIES OF STEEL. EFFECT OF STRUCTURE AND ALLOYING ELEMENTS

Steels to be employed for making machine parts, building structures and the like should possess high mechanical properties. A material for making machine parts to be subjected to high loads should exhibit sufficient strength and at the same time have an appropr iate ductility in order to resist dynamic and impact loads. In other words, the material should be highly strong and reliable.

In elements subjected to alternate loads, the metal should have a high fatigue resistance and in elements subjected to wear, a high wear resistance. In many cases a high corrosion resistance is essential, as well as the resistance to creep and other actions. This means that the elements made must have a high durability.

Thus, machine parts must be made of a strong, reliable and durable material.

Among all materials known in engineering, steel offers the best combination of strength, reliability and durability and for that reason is the principal material for making critical elements to be subjected to high loads.

The mechanical properties of steel depend on its structure and composition. The combined action of heat treatment and alloying is an effective means for improving the mechanical characteristics of steel.

Among the possible methods for improving (enhancing) the mechanical properties of steel are increasing of the carbon content; alloying; dispersion of structural components (by lowering the point of austenitic transformation, combined with tempering); grain refinement; and strain hardening.

Any strengthening effect performed by one of these methods (except for grain refinement and alloying with nickel) lowers the toughness (i.e. increases the ductile-to-brittle transition temperature and lowers the work of crack propagation).

Therefore, when developing the compositions of structural steels and conditions of heat treatment, preference should be given to methods which have the least effect on the plasticity and toughness of steel.

A simple increase of the carbon content in the ferrite-pearlitic structure (normalized state) can increase the strength and the ductile-to-brittle transition point. The maximum strength of this structure is attained at approximately 1% C and is only 100 kgf/mm² (see Fig. 7.1), whereas the ductile-to-brittle transition point is below 0°C only if the carbon content is not more than 0.4 per cent.

Thus, we can conclude that the maximum content of carbon in ferrite-pearlitic steel (without heat treatment) is 0.4 per cent; the steel will then have: $\sigma_t = 60$ kgf/mm², $T_{50} = -20$°C, and $a_p =$ = 6-7 kgf m/cm²*.

If a good weldability is additionally required of a steel, the content of carbon should be lowered to 0.2 per cent (to prevent cracking and embrittlement of weld seams); the strength will then drop down to approximately 35 kgf/mm².

The formation of disperse structures through undercooling of austenite can result in continuously increasing hardness and strength; the maximum hardness (strength) is exhibited by martensitic structure. With 0.4% C, martensitic structure has a hardness of about 60 *HRC* (650 *HB*), which corresponds to a strength of about 220-240 kgf/mm² [1]. The toughness of the metal is then intolerably low and must be increased by tempering, which, however, lowers somewhat the strength.

Two-stage heat-treatment, in which the final structure is formed from martensite rather than from austenite, i.e. hardening followed with tempering, makes it possible to vary the strength properties of steel within a wide range from the maximum value in as-hardened state to the minimum in as-annealed state; it is important that a steel thus treated has better plasticity and ductility properties than after ordinary treatment (products of decomposition of austenite).

This may be clearly seen from Table 16.1. For instance, if a steel has been treated to obtain its ultimate strength at a level of 80 kgf/mm², it turns out that its other characteristics after two-stage heat treatment (hardening + tempering) will be: $\delta = 26$ per cent; $\psi = 65$ per cent, and $a_{n_I} = 14$-17 kgf m cm², and after ordinary heat treatment (normalizing): $\delta = 14$ per cent, $\psi = 22$ per cent, and $a_{n_I} = 3$-6 kgf m/cm².

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* Let it be recalled that the ultimate strength σ_t characterizes the strength of steel (with ferrite-pearlitic structure, $\sigma_y = 0.5$-$0.6\sigma_t$); the ductile-to-brittle transition temperature T_{50} is the temperature at which there will be 50 per cent of ductile component in a fracture; and the work of crack propagation a_p is numerically equal to the impact toughness of a cracked specimen. Note that T_{50} characterizes the resistance of steel to brittle fracture and a_p, the resistance to ductile fracture. The values of toughness correspond to normalized steel Grade 40 of common purity and common grain size (grain size No. 5 to 8).

[1] In tensile tests, high-hardened steels (*HRC* > 58) show a lower strength than the value given here (owing to premature brittle fracture).

Table 16.1. Mechanical Properties of Steel

Ultimate strength σ_t, kgf/mm²	Yield strength $\sigma_{0.2}$, kgf/mm²	Elongation δ, %	Reduction ψ, %	Impact toughness a_n, kgf·m/cm²
Upon hardening and tempering				
160	140	10	45	4-6
140	120	15	50	6-7
120	100	18	50	7-9
100	85	21	55	10-12
90	80	23	60	12-14
80	70	23	65	14-17
70	60	30	70	18-22
Without heat treatment (or upon ordinary heat treatment)				
100	60	6	15	1-2
90	55	10	18	2-3
80	55	14	22	3-6
70	45	18	30	5-10
60	40	22	40	8-12
50	35	30	55	10-15

This difference has resulted from the different position of the ductile-to-brittle transition point and different percentage of fibres in a fracture (80 per cent in hardened and tempered steel and 30 per cent in normalized steel)[1].

This improvement in the steel quality (it should be emphasized that it is quality, but not strength, that has been improved) produced by two-stage heat treatment (hardening + tempering) suggests that the method can be called *improvement* (or more properly, *thermal improvement*).

Nevertheless, the possibilities offered by thermal improvement are not unlimited. As with other strengthening methods, an increase in the strength of thermally improved steel is associated with a loss of toughness. Figure 16.1 shows how the work of crack propagation depends on ultimate strength in improved steel (type Х5М2СФ).

The minimum value of the work of crack propagation in machine parts is $a_p = 2$ kgf m cm^2. For a steel made by common process and after common heat treatment (curves *1* in Fig. 16.1), this limit is attained at $\sigma_t = 180$ kgf/mm^2 (with fully ductile fracture).

However, another unfavourable factor appears here: the ductile-to-brittle transition point raises above the room temperature, so that

[1] The values given relate to steel Grade 40 of common structure and purity.

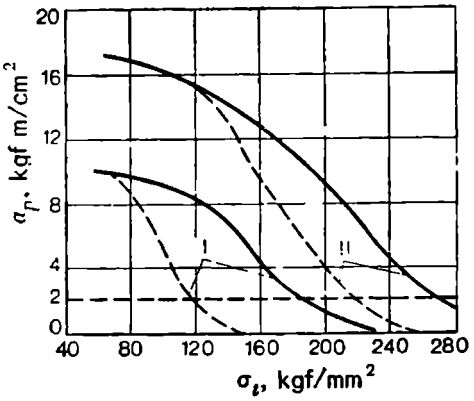


Fig. 16.1. Ultimate strength *versus* work of crack propagation. Steel type X5МФС, improved state (the author)

I — common purity, conventional heat treatment; *II* — high purity, refined grain (by HTHT); dotted lines — at 20°C; solid lines — at 300°C, 100-% ductile fracture

the percentage of fibres in a fracture decreases and the value of a_p (dotted line) also decreases. For that reason the highest ultimate strength (σ_t) of this steel at which a_p is still sufficiently high to ensure the required reliability, turns out to be only 120 kgf/mm^2.

It is then clear that the highest ultimate strength to retain an appropriate toughness is only 60 kgf/mm^2 after ordinary heat treatment (normalizing) and as high as 120 kgf/mm^2 after two-stage heat treatment (improvement).

Reasoning in the same way, we may conclude that the toughness of steel after isothermal bainitic hardening remains satisfactory at a strength not higher than 140-160 kgf/mm^2.

What is the role of alloying elements which, together with heat treatment, form a particular structure in steel? And how a particular value of strength is attained?

It follows from the foregoing that the optimal mechanical properties can be obtained by improvement (or isothermal hardening), for which purpose austenite should be undercooled in hardening to the temperature of martensite formation.[1] In carbon steels (Grades 20 to 40) using intensive quenchers (water), through hardening is possible in sections up to 10-15 mm thick.

It is impracticable to increase the hardenability by thermal means (more intensified quenching or grain coarsening) since there is a danger of formation of hardening defects and impairment of toughness.

Thus, there practically remains only one method for improving hardenability. This is alloying.

As has been found, addition of alloying elements first improves the mechanical properties of steel (for instance, the ductile-to-brittle transition point, see Fig. 16.2), until through hardenability is attained at given conditions (size of parts and cooling condi-

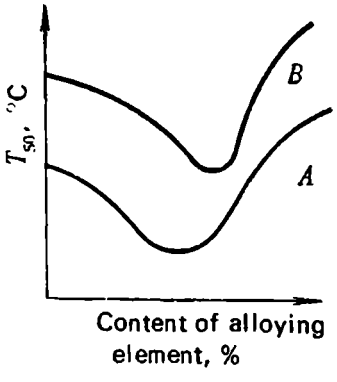


Fig. 16.2. Effect of alloying elements on ductile-to-brittle transition point

[1] Or to the temperature of bainite formation in isothermal hardening.

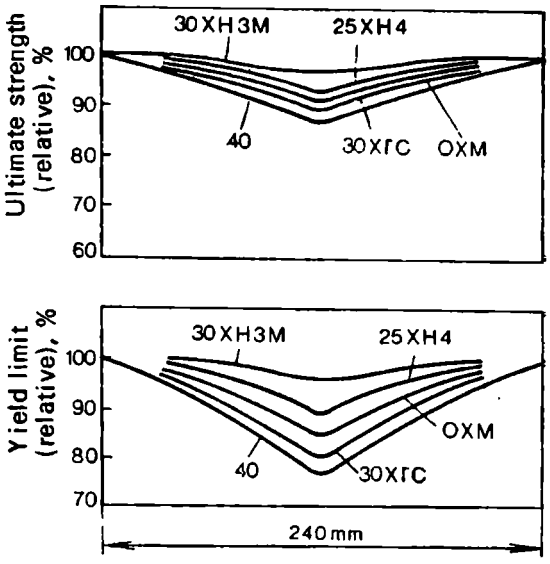


Fig. 16.3. Changes in mechanical properties over the cross-section of various steels upon improving heat treatment

tions); this corresponds to the minima of curves A and B in Fig. 16.2. After that, further increase in the content of an alloying element will impair the mechanical properties (steel B has a better hardenability than steel A)[1].

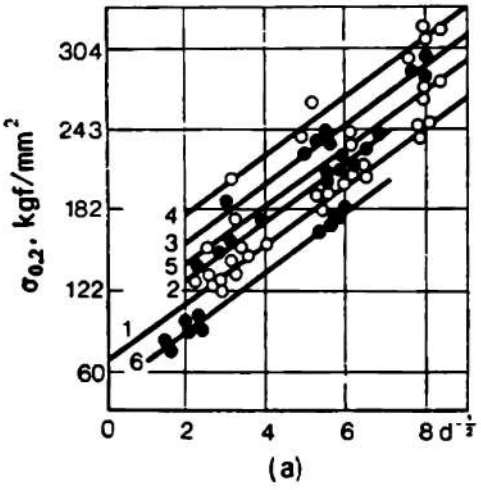
For these reasons, critical parts which are usually more than 10 mm in cross-sectional size are made of alloy steels and subjected to heat treatment. The greater is this size of a part, the more heavily alloyed steel should be employed (Fig. 16.3).

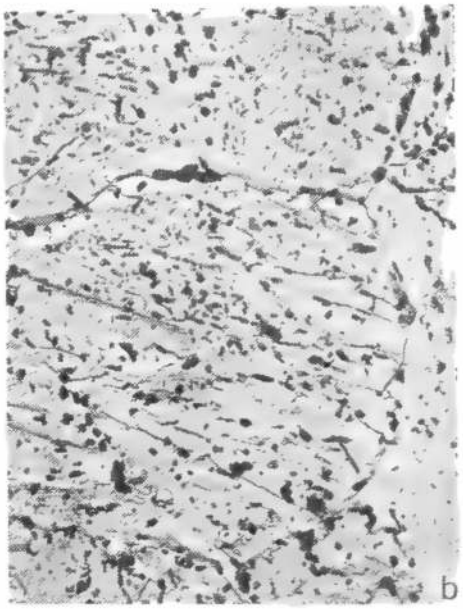
This would exhaust the role of alloying element[2], were it not for the circumstance as follows.

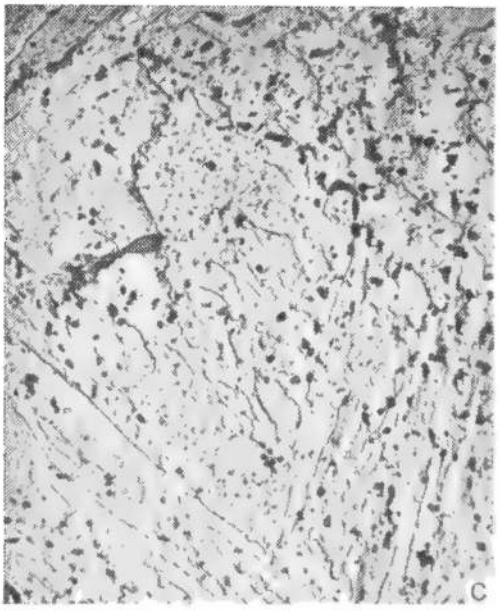
As may be seen from Fig. 16.1, the work of crack propagation at room temperature (dotted line *1*) is lower than the full value of a_p (solid line *1*), which is due to the appearance of a brittle component in the fracture. All alloying elements raise the ductile-to-brittle transition temperature and thus increase the content of brittle component in the fracture. The only exception is nickel which lowers the ductile-to-brittle transition temperature and inhibits brittle fracture. For that reason, alloyed structural steels for critical applications usually contain 1 to 3% Ni. The newest types of structural steel contain up to 9-18% Ni, mainly in order to lower the ductile-to-brittle transition point. Therefore, if a steel ruptured at room temperature has a 100-% ductile fracture, it will have the 'critical' value of $a_p = 2$ kgfm/cm^2 at a strength of 180 kgf/mm^2.

[1] As is known, alloying is done for a definite purpose (to increase hardenability, heat resistance, etc.). In most cases it turns out that there is an optimal content of a given alloying element above which the alloying effect is negative. The problem is dealt with in the *theory of ultimate alloying*.

[2] As was supposed by E.C. Bain (1940).







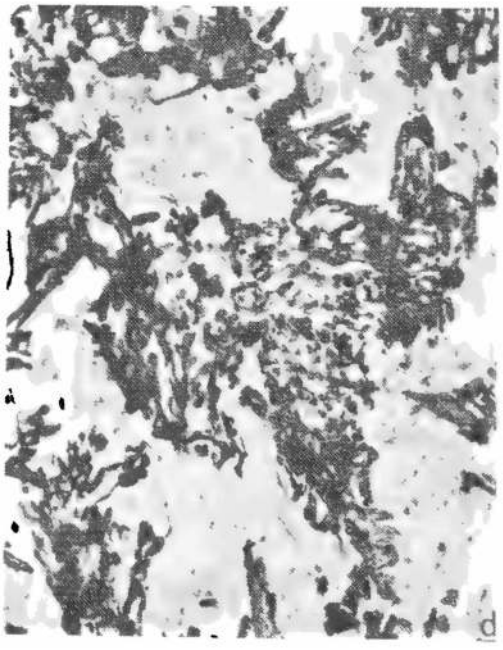


Fig. 16.4. Effect of grain size on yield limit (*a*) and the microstructures of carbides upon high-temperature tempering (650°C) with the initial structure of martensite (*b*), lower bainite (*c*), upper bainite (*d*). ×7 700

1-6 — various steels; *d* — grain size

Indeed, as has been found by experience, high-nickel steels show no brittle fracture at room temperature and can serve reliably at σ_t = 160-180 kgf/mm^2.

Are there any prospects for further increase of the strength at the required level of reliability (a_p = 2 kgf m/cm^2)?

Refinement of steel from harmful impurities (the use of a cleaner charge combined with advanced remelting processes) can increase the toughness[1] (curves *II* in Fig. 16.1) at a given strength. Thus, the use of high-purity steels is a real method for utilizing an elevated strength (at $\sigma_t > 180$ kgf mm^2) or saving nickel (at $\sigma_t < 180$ kgf/mm^2).

Another method for utilizing (increasing) the high strength is grain refinement. Refinement of ferritic grain can raise the yield limit[2] (Fig. 16.4) and at the same time can give another positive effect: lower the ductile-to-brittle transition temperature, i.e. increase the resistance to brittle fracture.

Refinement of steel from harmful impurities, when combined with grain refinement by high-temperature thermomechanical treatment (HTHT), can raise a_p and practically form conditions for using steels with σ_t = 220-240 kgf/mm^2 (curves *II* in Fig. 16.1).

Intensive work is being carried out for obtaining steels with extra-fine grain (Nos. 12 to 14, i.e. a few micrometres in diameter). This will increase the reliable level of steel strength.

Apart from having a high strength, structural steels must also possess some other important properties: rigidity, reliability, durability; all these factors determine both the selection of material and the dimensions of the parts made of them.

For instance, the rigidity of a structure is determined by the normal elastic modulus (E) of steel, whereas the dimensions of a steel part are determined by the value of that modulus and the allowable elastic deformation.

In order to avoid residual deformation in an element under operating load, the rated stress in it should not exceed the yield limit. Thus, the yield limit ($\sigma_{0.2}$) also determines the dimensions of an element.

The reliability of an element, i.e. a guarantee that it will not break occasionally, is higher at a higher resistance to fracture (which is determined by T_{50}, a_p, and K_{Ic}).

The durability of an element is determined by the resistance of its material to wear, corrosion, creep, etc. and is characterized by the time (duration) of normal operation.

In many cases all these characteristics cannot be determined sufficiently accurately for elements of a given shape and for given operating conditions; in such cases the dimensions and mass of elements are determined approximately on the basis of 'design considerations'.

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[1] That is, lower T_{50} and increase a_p.

[2] The effect of refinement of ferritic grain on yield limit can be characterized by what is called the Petch-Hall formula (Fig. 16.4): $\sigma_{0.2} = \sigma_0 + Kd^{1/2}$ (where $\sigma_{0.2}$ is the yield limit; σ_0 is the yield limit of a very coarse-grained metal; K is a coefficient; and d is the size of grains). By the latest data, however, the formula is incorrect, since the yield limit depends on the internal (fine) structure of grains, as well as on grain size.

16.2. HEAT TREATMENT OF STRUCTURAL STEELS

As may be seen from Table 16.1, two-stage heat treatment of alloy steel gives higher mechanical properties for the same strength level. This is why alloy steels which are much more expensive than common steels, must be used in structures exclusively after heat treatment[1].

The conditions of heat treatment of structural steels are determined mainly by the carbon content.

We consider the typical conditions of heat treatment for low-carbon (0.10-0.25% C) and medium-carbon (0.30-0.45% C) structural steels, which are used most commonly in practice.

Structural steels are usually subjected to two-stage strengthening heat treatment (hardening + tempering), with medium-carbon steels being subjected to high-temperature tempering (improvement) and low-carbon grades, to low-temperature tempering.

The conditions of hardening are determined by the position of the critical points and the capability of austenite for being undercooled.

Heating for hardening is commonly done to a temperature slightly (by 30-50 deg C) exceeding the Ac_3 point. This temperature is near 900°C for most grades of low-carbon structural steels and 850°C, for medium-carbon steels.

Like carbon steels, low-alloy steels should be quenched in water (only small-size elements should be oil-quenched), since quick cooling is essential in view of the low stability of undercooled austenite in the region of pearlitic breakdown (near 600°C).

As we already know, an increase in the content of alloying elements increases the stability of undercooled austenite. In structural steels of common composition, the content of alloying elements is such that the steels can be quenched in oil. In some complex-alloyed steels (for instance, in Cr-W and Cr-Ni-Mo steels), the pearlitic transformation is retarded to such an extent that the austenite can be undercooled to the temperature of martensitic transformation simply by cooling large-size elements in quiet air.

Considering the conditions to be created for quenching of alloyed structural steels, we should recall still another particularity of the kinetics of austenitic decomposition in steels alloyed with carbide-forming elements. In such (low-carbon) steels, the rate of bainitic transformation at 300-400°C turns out to be substantially higher than the rate of pearlitic decomposition (500-600°C), (Fig. 14.12). Thus, cooling within the lower temperature range (at 300-400°C) should be accelerated in order to avoid bainitic transformation.

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[1] With the exception of some grades of constructional steel alloyed with small amounts of cheap elements—manganese and silicon; these can in some cases be used without heat treatment.

This statement can be corrected, however, in view of the latest research data.

As has been given earlier, the region of bainitic transformation comprises upper and lower bainite. A high toughness upon improving heat treatment (high-temperature tempering) is due to the precipitation of uniformly distributed disperse carbides. This can be achieved with the initial martensitic structure and the structure of lower bainite (Fig. 16.4*b* and *c*).

With the initial structure of upper bainite, carbide inclusions are coarse and of the lamellar form and impair appreciably the toughness (Fig. 16.4*d*).

Therefore, for effective improvement upon hardening, the structure should be martensitic or martensite + lower bainite. The formation of upper bainite in an appreciable concentration in hardened products (prior to tempering), as also of ferrite or pearlite, impairs the toughness properties: raises the ductile-to-brittle transition temperature and lowers the impact toughness.

As a general conclusion, it may be noted that martensitic structure can be formed in alloy steels by a slower cooling than in carbon steels; a slower cooling causes lower internal stresses, and therefore, increases the structural strength.

Hardening of steel to martensite is the first stage in the heat treatment of structural steels. Structural steels cannot be used in as-hardened state in view of the low ductility and appreciable internal stresses. They should be then subjected to tempering which increases the ductility and toughness and reduces internal stresses.

Tempering is the concluding operation of heat treatment of structural steels; it forms the final properties of the steel.

Let us consider how the temperature of tempering influences the mechanical properties of steel, taking as examples low- and medium-carbon Cr-Ni steels (Fig. 16.5).

In both cases, the ultimate strength (σ_t) diminishes and the ductility (relative reduction in our case) increases with the temperature of tempering.

In the low-carbon steel, martensite is quite plastic after hardening. Tempering at 150°C removes (naturally, only partially) the internal stresses and increases somewhat the ductility. In best grades of low-carbon alloy steels, this mode of heat treatment (hardening + tempering at 150°C) provides a high complex of mechanical properties (σ_t up to 130-140 kgf/mm^2, ψ = 50-60 per cent, and a_{n_I} up to 12-14 kgf m/cm^2). The structure of the steel upon this heat treatment is a tempered low-carbon martensite.

In the medium-carbon structural steels, where the martensite has a higher carbon content upon hardening, this mode of tempering is insufficient if a high toughness of the steel is essential.

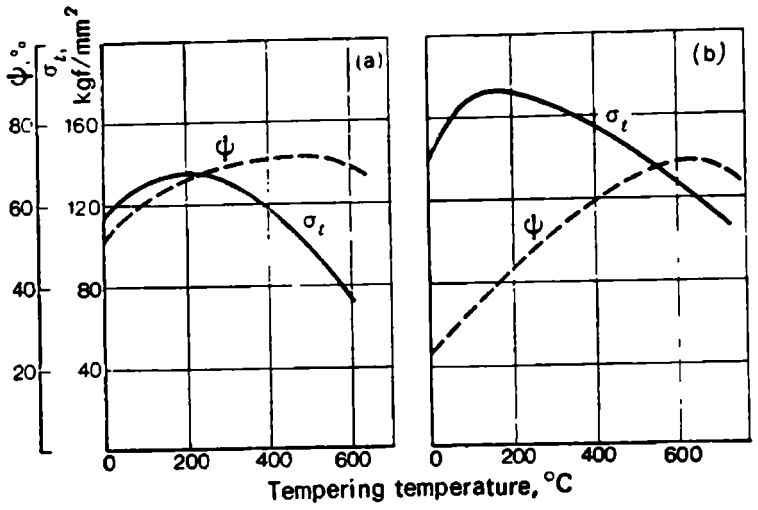


Fig. 16.5. Effect of tempering on the mechanical properties of Cr-Ni steel (*a*) low-carbon grade; (*b*) medium-carbon grade

With low-temperature tempering, the steel will have an elevated strength (σ_t = 160-170 kgf mm^2) and low values of ductility and toughness. This is why these steels should be tempered at a higher temperature, usually at 550-600°C. At this temperature, martensite decomposes completely and forms a granular high-disperse ferrite-carbide mixture—sorbite. The mechanical properties will then be roughly the same as in low-carbon steels upon low-temperature tempering, i.e. σ_t = 120-130 kgf mm^2, ψ = 50-60 per cent, and a_{n_I} = = 12-14 kgf m/cm^2.

Thus, we can draw certain conclusions.

The typical conditions of heat treatment to botain the best complex of mechanical properties are as follows: for low-carbon alloy steels—hardening from 900°C with oil quenching and tempering at 150°C (the structure of tempered martensite); for medium-carbon alloy steels—hardening from 850°C with oil quenching and tempering at 550-650°C (the structure of sorbite). In both cases the mechanical properties obtained are almost the same.

In some cases, these typical conditions of heat treatment are changed somewhat.

For instance, high-alloyed low-carbon steels are sometimes tempered at a higher temperature, which is done to obtain higher ductility and toughness (at a somewhat lower strength).

Medium-carbon steels are tempered at 200-250°C when an especially high strength (σ_t = 160-180 kgf/mm^2) is required; this however gives a relatively low impact toughness (a_{n_I} = 4-6 kgf m/cm^2 and a_p = 1-2 kgf m/cm^2).

In some steels, a combination of high strength and high ductility (σ_t = 140-170 kgf/mm^2, a_{n_I} = 6-7 kgf m/cm^2) can be obtained by isothermal hardening with decomposition of austenite in an intermediate temperature interval (300-400°C).

The highest strength can be achieved through thermo-mechanical treatment (Sec. 10.8), though the process is rather complicated technologically.

Consider now the effect of tempering temperature and the cooling rate after tempering on the impact toughness of alloy structural steels (Fig. 16.6).

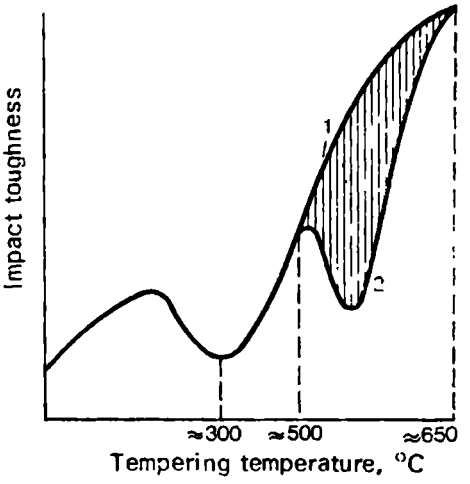


Fig. 16.6. Effect of tempering on the impact toughness of alloy steel (schematic)
1 — quick cooling; *2* — slow cooling

For the case of slow cooling after tempering, the curve of impact toughness has two minima: for tempering at 300°C and approximately at 550°C.

Embrittlement of steels under certain tempering conditions is called *temper brittleness*. The loss in toughness here is associated with an increase in the ductile-to-brittle transition temperature. Two types of temper brittleness are distinguished.

First-order temper brittleness appears in all steels on tempering at temperatures near 300°C, irrespective of the steel composition and the cooling rate upon tempering.

What are the probable causes of the first-order temper brittleness?

There are several explanations to this phenomenon. It has been supposed, for instance, that embrittlement is associated with the disappearance of the ductile phase—retained austenite, which at these temperatures transforms into temper martensite (second transformation on tempering). This assumption, however, disagrees with the fact that first-order brittleness is also observed in cases when the structure contains no retained austenite on hardening.

By another assumption, embrittlement is mainly due to a lamellar shape of precipitated carbides. It is well known, however, that lamellar carbides are formed in tempering before the appearance of brittleness and that they remain in the structure at higher temperatures when the toughness of the steel is restored.

By a recent assumption, temper brittleness is due to non-uniform decomposition of the supersaturated solid solution of carbon in α-iron (in temper martensite). At these temperatures, the decomposition occurs most completely (almost to the end) at grain boundaries, resulting in a sharp difference between the strength of the boundary layers of grains and that of grain bodies. In that case, the less strong boundary layers serve as stress concentrators and cause brittle fracture. With an increased time of tempering or a higher tempering temperature, the degree of decomposition of α-solution should be equalized over grains and the steel should regain its initial toughness.

Second-order temper brittleness is found in steels tempered at temperatures above 500°C. Its specific feature is that it appears after slow cooling on tempering; with quick cooling, toughness is not decreased, but increases monotonously with increasing temper temperature (see the upper curve in Fig. 16.6). Second-order temper brittleness can however be again caused by a new high-temperature tempering with subsequent slow cooling[1].

It should be noted that all other mechanical properties of a steel are practically independent of the cooling rate upon tempering.

Not all steels are susceptible to second-order brittleness. It does not appear in carbon steels. Steels alloyed with carbide-forming elements (manganese, chromium) are susceptible to second-order brittleness in the presence of more than 0.001% P. Chromium makes a steel highly sensitive to the cooling conditions on tempering, especially when the steel also contains nickel or an elevated percentage of manganese. Thus, manganese and phosphorus increase this susceptibility, whereas molybdenum and, to a lesser extent, tungsten depress it.

Experiments have shown that if an alloy steel which has been cooled quickly after tempering at 650°C is again heated for a long time at 500-520°C, it will become brittle irrespective of the rate of subsequent cooling. Therefore, certain diffusion processes develop in the steel at temperatures below 600°C and cause embrittlement.

What is the nature of second-order brittleness?

It has been demonstrated metallographically that development of second-order brittleness is associated with precipitation of excess phases at grain boundaries.

It has also turned out that grain boundaries may be enriched with phosphorus, which effect is revealed by etching with picric acid (Fig. 16.7*a*). The same etching of the steel in ductile state fails to reveal grain boundaries (Fig. 16.7*b*).

An explanation of the phenomenon of second-order brittleness (L.M. Utevsky) is briefly as follows.

With high-temperature tempering, carbide formation occurs more quickly at grain boundaries (than in the body of grains), where the carbide phase becomes saturated with manganese and chromium, and special carbides are also formed (if the steel has been properly alloyed). This process results in the boundary layers of grains being depleted of carbide-forming elements. With subsequent slow cooling (or during soaking at 500-520°C), these boundary layers are enriched with phosphorus, since phosphorus at temperatures below 600°C has a tendency for diffusional redistribution in the direction of the portions depleted of carbide-forming elements (the phenomenon of ascending diffusion) and the diffusion mobility of phosphorus atoms at these temperatures is sufficiently high. In the final analysis, the steel is embrittled owing to the weakening of intergranular bonds.

This brittleness can be eliminated by a new tempering followed by quick cooling. This occurs since the former non-uniformity of phosphorus distribution can be retained at temperatures above 600°C and the concentration of phosphorus

[1] For that reason, second-order temper brittleness is sometimes called *reversible temper brittleness* and first-order temper brittleness, *irreversible*.

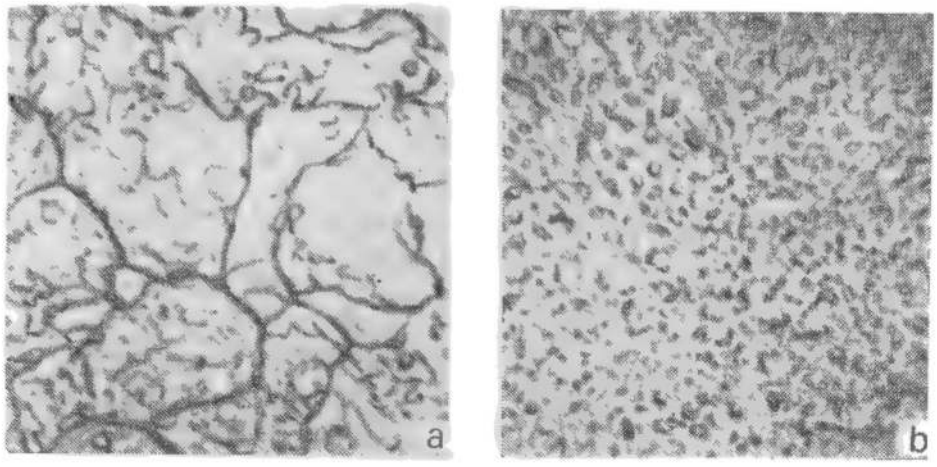


Fig. 16.7. Microstructure of Cr-Ni steel as-tempered at 550°C. ×500
(*a*) slow cooling, brittle state; (*b*) quick cooling, ductile state

is equalized. With subsequent quick cooling, phosphorus has no time for redistribution at temperatures below 600°C and cannot saturate grain boundaries.

The favourable effect of small additions of molybdenum (up to 0.5-0.6%), which can retard and sometimes even prevent second-order brittleness, can be explained by the fact that molybdenum only weakly participates in the formation of alloyed cementite $(Fe, Mo)_3C$ and at these low concentrations forms no special carbides. For that reason, boundary portions of grains are not depleted of molybdenum. The presence of molybdenum in the solution, however, diminishes the difference in the diffusion mobility of atoms at the boundaries and in the body of grains and thus hampers non-uniform distribution of other carbide-forming elements. Besides, molybdenum neutralizes the harmful effect of phosphorus at grain boundaries.

At a higher concentration, molybdenum can form a special carbide in steel. This will result in depletion of grain boundaries of molybdenum during tempering and in their enrichment in phosphorus during subsequent slow cooling. Therefore, molybdenum in higher concentrations will induce the development of temper brittleness. A similar effect is produced by tungsten.

It follows from what has been said above that embrittlement can be avoided by cooling the metal as quickly as possible through the temperature range of the first-order temper brittleness (300-400°C). For steels susceptible to the second-order temper brittleness, quick cooling on tempering is essential. These steels should not be heated to high temperatures (500-600°C) during operation, since this might cause their embrittlement. In cases when quick cooling on tempering is impossible (for instance, with very large steel parts) it is advisable to employ molybdenum-alloyed steels in which the development of second-order temper brittleness is retarded.

The use of steels pure from phosphorus, interstitial impurities (oxygen, nitrogen, hydrogen) and non-ferrous metals (tin, etc.) is a more effective means for preventing second-order temper brittleness than the additional alloying with molybdenum or tungsten.

16.3. CEMENTABLE (LOW-CARBON) STEELS

Let us consider the most common low-carbon steels used for making cemented parts. As has been indicated, the steels used for the purpose have a low carbon content (0.1-0.25%) so as to obtain a hard surface layer and tough core after cementation, hardening and low-temperature tempering. The hardness of the surface will be around 60 *HRC* and that of the core, 15-30 *HRC*.

Steels of this type have a low hardenability, so that only a thin surface layer is hardened, but not the core.

On the other hand, alloy steels upon heat treatment (hardening — low-temperature tempering) are hardened in the core, the effect being greater in steels containing more of carbon and alloying elements.

In that connection, cementable steels should be classed into three groups: carbon steels giving unhardened core upon heat treatment;

Table 16.2. Composition of Cementable Steels [1], % (GOST 4543-71)

Nos.	Steel Grade	C	Cr	Ni	Mn
1	10	0.07-0.13	—	—	—
2	20	0.17-0.24	—	—	—
3	15X	0.12-0.18	0.8-1.0	—	—
4	20X	0.17-0.23	0.7-1.0	—	—
5	15XP	0.12-0.18	0.7-1.0	—	—
6	20XH	0.17-0.23	0.45-0.75	1.0-1.4	—
7	20XГP	0.18-0.24	0.7-1.1	—	0.7-1.0
8	20XHP	0.16-0.23	0.7-1.1	0.8-1.1	—
9	18XГT	0.17-0.23	1.0-1.3	—	0.8-1.1
10	30XГT	0.24-0.32	1.0-1.3	0.6-0.9	—
11	18XHMФA	0.16-0.21	0.6-0.9	—	0.8-1.1
12	12XH3	0.09-0.16	0.6-0.9	2.75-3.15	—
13	12X2H4	0.09-0.16	1.25-1.65	3.25-3.65	—
14	20X2H4	0.16-0.22	1.22-1.65	3.25-3.65	—
15	18X2H4B*	0.14-0.20	1.35-1.65	4.0-4.4	—

[1] All the steels mentioned contain up to 0.8 % Mn (or more where indicated), 0.17-0.37 % Si, and not more than 0.035% S and P. In high-quality steels (designated by a letter A), the content of S and P does not exceed 0.025 %. Steels with a letter T in the designation have a specified content of titanium within 0.06-0.12 %; those without this letter contain 0.01-0.03 % titanium, which is introduced for deoxidation. Steels designated by a letter P have a specified content of 0.002-0.003 % B. Steel Grade 18XHMФA additionally contains 0.08-0.14 % V.

* Also contains 0.45-0.65% Mo or 0.8-1.2 % W.

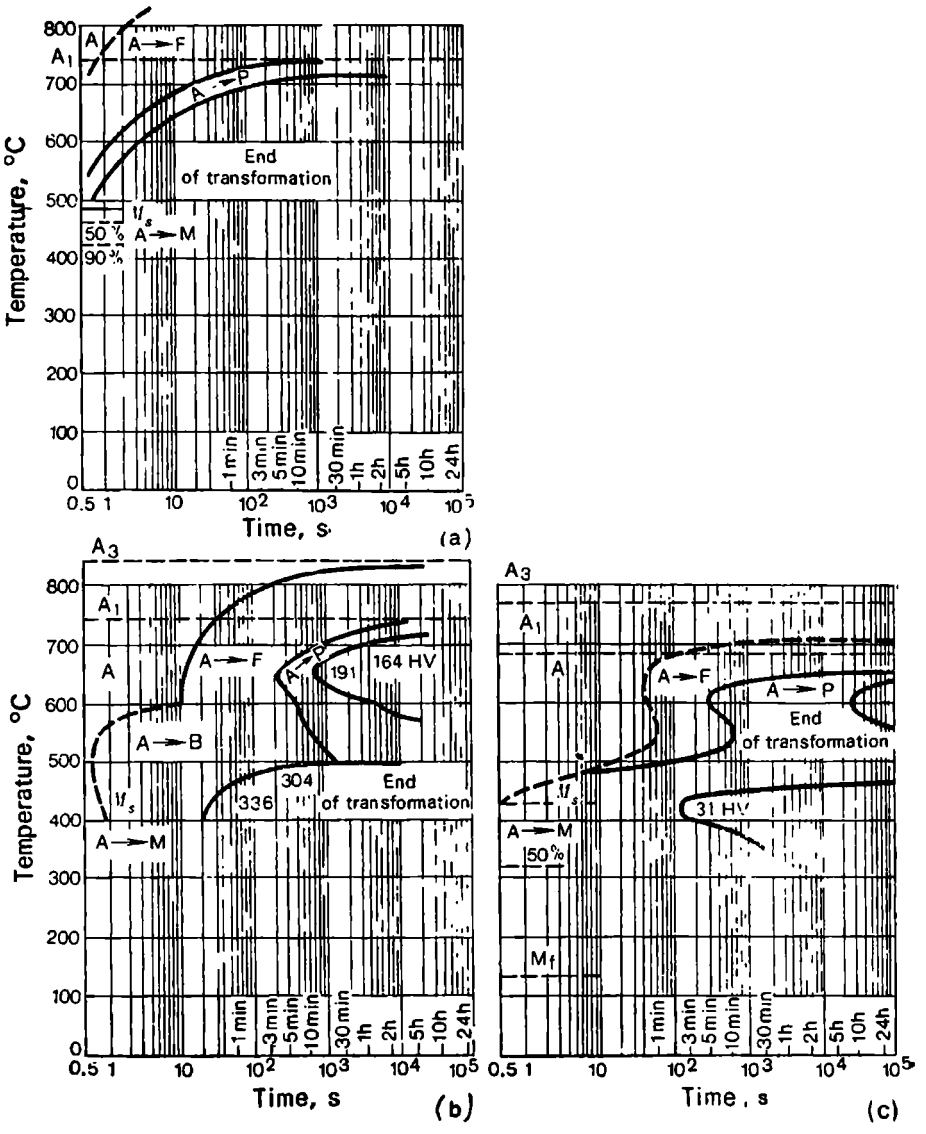


Fig. 16.8. Diagram of isothermal decomposition of austenite in cementable steels (*a*) steel 10; (*b*) 20ХГ; (*c*) 12Х2Н4 (A. A. Popov)

low-alloy steels with weakly hardened core; and more heavily alloyed steels in which the core is strongly hardened upon heat treatment. Steels of the last group are sometimes called high-strength cementable steels. They also include steels having a relatively low content of alloying elements and an elevated content of carbon (0.25-0.30%).

The compositions of the most common grades of cementable steel are given in Table 16.2.

The kinetics of decomposition of undercooled austenite in these steels may be different (Fig. 16.8), resulting in different structures formed upon heat treatment and different hardening effect.

With non-alloyed low-carbon steels (such as steel Grade 10), the nose of the C-shaped curve (Fig. 16.8*a*) is so shifted to the left that in layers below the

cemented layer the austenite cannot be undercooled even by severe quenching in water. Practically, the austenite transforms into ferrite-pearlitic mixture irrespective of cooling conditions. This type of steel shows almost no strengthening effect on heat treatment.

The diagrams of isothermal decomposition of austenite in low-carbon low-alloy steels are characterized by a greatly developed region of intermediate bainitic transformation (Fig. 16.8*b*). In oil quenching, if the intensity of cooling has been sufficient to form a high hardness in the cemented surface layer, the core undergoes bainitic transformation and is strengthened noticeably.

Finally, with high-alloyed cementable steels, quenching in oil or even air cooling is sufficient to form the structure of lower bainite or martensite in the core (Fig. 16.8*c*), which results in an appreciable strengthening effect.

Thus, the above division of cementable steels into three groups corresponds to the structure formed in the core (upon oil quenching), which may be ferrite-pearlitic, bainitic or martensitic.

As has been given, the first group includes carbon steels Grades 10, 15, and 20 (see Table 16.2), which are widely used for making cemented steel parts. These inexpensive steels are used for making steel parts which should have a high resistance to wear and not very high strength. The depth of cementation is selected depending on the operation conditions[1]. After cementation, the steel parts are hardened in water and tempered at 150-180°C. Water quenching can cause strong deformation of steel parts. The mechanical properties of cementable carbon steels are given in Table 16.3.

Table 16.3. Mechanical Properties[1] of Cementable Carbon Steels

Steel Grade	σ_t, kgf/mm²	σ_y, kgf/mm²	δ, %	ψ, %
10	40	25	35	70
15	43	27	32	65
20	47	30	30	60

Note. Impact toughness is not given in the table. It may vary after case hardening within very wide limits depending on the actual grain size, which in turn depends on the conditions of case hardening and the subsequent heat treatment in which the initial grain size is restored.

[1] The table gives the most typical values of mechanical properties. GOST's (or technical specifications) usually give somewhat lower values; the same relates to Tables 16.4 and 16.5.

The second group includes low-alloy steels and those which can be strengthened by heat treatment, in particular, Grades 15X, 15XP and 20XH (see Table 16.2).

The properties of these steels in as-annealed state are practically the same: σ_t = 50-60 kgf/mm², $\sigma_{0.2}$ = 34-40 kgf/mm², δ = 30 per cent, ψ = 60 per cent, and hardness 140-180 *HB*.

Upon hardening and low-temperature tempering, the strength of low-alloy steels increases noticeably, with only a slight loss of ductility (Table 16.4).

[1] The thickness of cemented layer is determined by the unit pressure on the surface in operation.

Table 16.4. Mechanical Properties of Cementable Alloy Steels

Steel Grade	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %	ψ, %	a_{nI}, kgf m/cm²
15X	75	65	15	55	10
20X	85	70	15	55	12
15XP	75	65	15	55	12
20XH	85	70	15	55	12

Note. After oil quenching and tempering at 200° C.

The properties indicated are characteristic of low-carbon steel of bainitic type.

Steels 20ХГР, 20ХНР, 18ХГТ, 30ХГТ, 12ХН3, 12Х2Н4, 18Х2Н4В should be related to the third group, that of high-strength cementable steels which are strengthened appreciably on heat treatment owing to the formation of martensite in the core upon hardening. The strengthening effect is determined by the content of carbon and also, though to a lesser extent, by the content of alloying elements and the intensity of cooling upon hardening.

Table 16.5 gives the mechanical properties of selected high-strength cemen-

Table 16.5. Mechanical Properties of Cementable High-strength Steels

Steel Grade	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %	ψ, %	a_{nI}, kgf m/cm²
20ХГР	130	110	12	50	8
20ХНР	130	110	14	60	9
18ХГТ	130	110	12	50	8
30ХГТ	160	140	10	40	7
18ХНМФ	120	100	15	55	16
12ХН3	120	100	15	60	10
12Х2Н4	120	110	15	60	10
18Х2Н4В	130	110	14	55	10

Note. Upon oil quenching and tempering at 200° C.

table steels. It should be considered that the effect produced by increasing the carbon content (within the limits specified for a steel grade) and the quenching rate in hardening is not only an increased strength, but also reduced values of ductility and toughness.

High-strength cementable steels are used for making steel elements of which a high reliability and high resistance to dynamic loads are required; the elements are case-hardened to a shallow depth.

The mechanical properties of these steels in as-annealed state (tempered at 650-680°C) are roughly of the same order as those of the less strong grades of cementable steel.

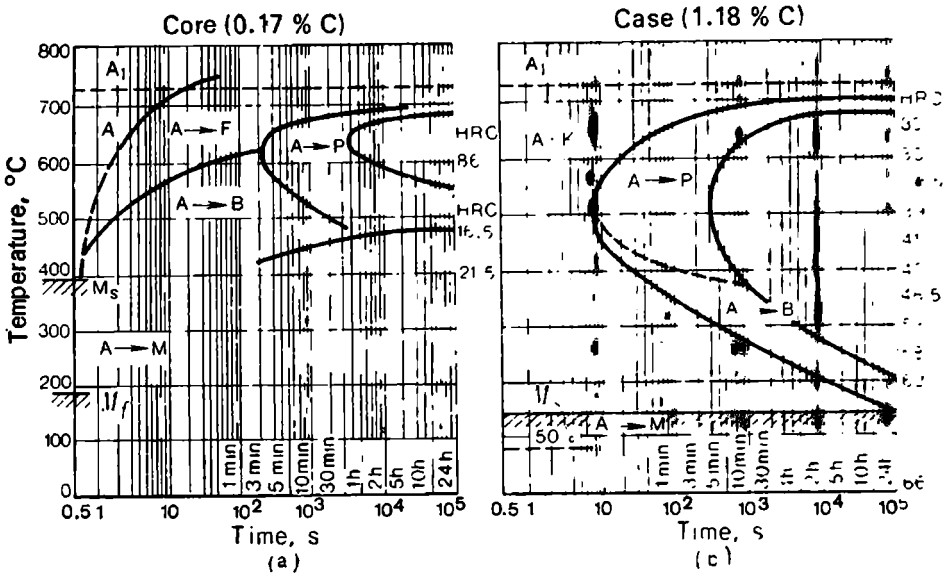


Fig. 16.9. Diagram of isothermal decomposition of austenite in steel 20XHM

The mechanical properties of steels, as given in the tables above, relate to the core of a case-hardened part. If the properties of the whole case-hardened part are determined, the hard cemented case will turn out to have an appreciably lower toughness and a higher strength compared to the respective properties of the core. The difference between the properties of the hardened case and the core depends on many factors, in the first place, on the strength level in the core, the relative area of the cemented layer and core, the degree of saturation with carbon, etc.

As has been given, heat treatment of cemented parts for critical applications usually consists of hardening from a special heating (t_h = 800°C) and tempering (t_{tem} = 200°C). The processes occurring in the core and surface layer during heat treatment are different owing to the sharp difference in the carbon content.

Figure 16.9 shows curves of isothermal transformation in the austenite of steel Grade 20XHM for the surface layer (*b*) and the core (*a*). In the core, the transformation in pearlitic region begins from intensive formation of ferrite. The region of bainitic transformation is shifted to the left, so that a mixed bainite-martensitic transformation occurs in this steel during oil quenching or even air cooling[1].

With a high carbon content, the transformation in the pearlitic region occurs without the formation of ferrite; the rate of bainitic transformation is appreciably lower. Cooling in air or oil quenching causes purely martensitic transformation; since the position of the martensitic point is low (150°C), a large amount of retained austenite is fixed by hardening.

For the low-carbon core, the usual interval of martensitic transformation M_s-M_f is 350-200 deg C; for a high-carbon core, point M_s is at 100-200°C and M_f, below 0°C. Sub-zero treatment can cause no changes in the core of hardened cementable steel, whereas part of the retained austenite in the surface layer transforms to martensite.

Tempering at 150-200°C causes no structural changes in the core, but results in tempering of the tetragonal martensite in the surface layer.

[1] That is, the austenite is transformed partially into bainite and partially, into martensite.

Steel grades for case-hardened steel parts are selected from the following considerations.

Carbon steels of simple composition should be used for making parts of simple shape and not to be subjected to appreciable stresses; chromium-nickel high-strength steels are recommended for parts to be subjected to large stresses and impact loads. Various intermediate cases are possible between these two extremes.

Parts of intricate shape (such are gear wheels) should be made of alloy steels and quenched in oil to avoid hardening deformations.

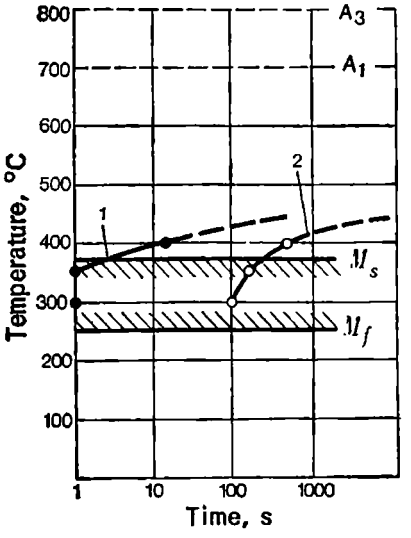


Fig. 16. 10. Diagram of isothermal decomposition of austenite in steel 18XH4BA (the author)

1 — beginning of transformation; *2* — end of transformation

Let us consider some examples.

The most critical cemented parts are made of chromium-nickel and chromium-nickel-tungsten steels 12X2H4A and 18X2H4BA. These steels acquire very high mechanical properties (ultimate strength up to 120-140 kgf/mm²) upon hardening and low-temperature tempering. For that reason, these steels (especially Grade 18X2H4BA) are also often used without case-hardening (in parts requiring high strength but no especially high wear resistance).

Steel Grade 18X2H4BA has a peculiar diagram of isothermal breakdown of austenite where there is no region of pearlitic decomposition and the interval of bainitic transformation almost coincides with that of martensitic transformation (Fig. 16.10).

As may be seen from the diagram, the critical point[1] A_1 lies at 700°C and A_3, at 800°C. There is no pearlite-troostitic decomposition (at 500-700°C) in this steel, and its austenite can transform either into bainite (within the range of 450-300°C) or into martensite (with quick continuous cooling).

The temperature range of martensitic transformation is roughly within the following limits: the beginning (point M_s) at 370°C and the end (point M_f) at 250°C. The high position of point M_f is favourable in that only a slight amount of retained austenite (roughly 2-4%) is formed in this steel on hardening.

The diagram of isothermal transformation in steel Grade 18X2H4BA also shows that this steel must not be annealed since its austenite cannot be transformed into pearlitic structures. For that reason, the sole method of softening heat treatment for this steel is high-temperature tempering 'under the critical point' (660° ± 10°C). The structure of the steel upon this heat treatment (as delivered) is sorbite with a non-uniform distribution of carbon (Fig. 16.11*a*).

This kinetics of austenitic decomposition in the steel is responsible for the fact that, with any method of cooling (even very slow cooling) and practically in any cross-section, the austenite is undercooled to the temperatures of bainitic and martensitic transformation, because of which steel Grade 18X2H4BA can be through-hardened in any cross-section and practically can be referred to the class of martensitic steels.

[1] The critical points of this nickel-alloyed steel are lower compared with plain carbon steel.

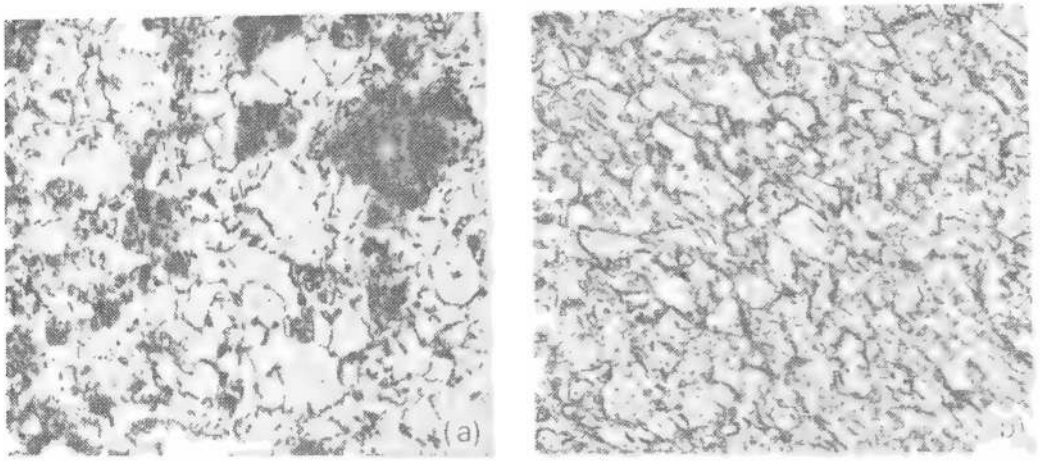


Fig. 16.11. Microstructure of steel 18XH4BA. ×500
(*a*) as delivered; (*b*) as hardened and tempered at low temperature

For the reasons mentioned, steel Grade 18X2H4BA is usually cooled in air (even in massive parts), rather than quenched in oil.

It should be noted, however, that partial bainitic transformation upon tempering impairs the mechanical properties of the metal. This is why slow cooling in the range from 400 to 200°C can have an adverse effect on the final mechanical properties.

The structure of steel Grade 18X2H4BA after conventional heat treatment, i.e. hardening plus low-temperature tempering, is low-carbon martensite. It is shown in Fig. 16.11*b*.

In view of the high content in alloying elements, the point M_f for the carbon-saturated case-hardened layer of steel 18X2H4BA is below 0°C. Therefore, the layer will contain an appreciable amount of retained austenite upon common hardening and low-temperature tempering and its hardness may often be below the allowable limit (58-62 *HRC*). A similar phenomenon is found in chromium-nickel steels 12XH3A and 12X2H4A.

An effective method for eliminating the excess of retained austenite from case-hardened layer is sub-zero heat treatment: hardened parts are cooled to a sub-zero temperature, which causes almost all of the austenite in the surface layer to transform into martensite; thus the hardness of the surface layer increases. The process does not change the properties of the core (which contains little carbon), since the quantity of retained austenite is not high and is not changed by cooling at sub-zero temperatures.

Nitriding of this steel (see Sec. 13.3) has found use recently for increasing the durability.

16.4. IMPROVABLE (MEDIUM-CARBON) STEELS

Improvable steels contain 0.3-0.4% C and various amounts of alloying elements (chromium, nickel, molybdenum, tungsten, manganese, silicon) totalling not more than 3-5 per cent; they are often alloyed with around 0.1 per cent of grain-refining elements (vanadium, titanium, niobium, and zirconium).

The common heat treatment of these steels is hardening with oil quenching and high-temperature tempering (at 550-650°C).

The hardenability of these steels depends directly on the content in alloying elements.

Since the mechanical properties of various grades of steel in this group upon heat treatment (with through hardening) are very close, the selection of a particular steel grade for a particular part is determined by the hardenability, rather than by mechanical properties.

Parts of larger cross-section require a more heavily alloyed steel grade. It is advisable to employ molybdenum-alloyed steels (0.15-0.30% Mo) to avoid the development of temper brittleness, which is especially dangerous in large parts that cannot be cooled quickly on tempering.

Parts of intricate shape, especially those to be subjected to impact loads, should be preferably made of nickel-containing steel grades.

The compositions of the commonest steels in this group are given in Table 16.6.

The improvable steels are conditionally divided into five groups. The degree of alloying and, therefore, the size of through-hardened cross-section increase with increasing group number.

Group I includes plain carbon steels. They are usually employed in normalized state or without heat treatment[1]. The properties of steels in this state have been discussed earlier (see Secs. 16.1 and 16.2). In some instances, in particular, in parts 10-15 mm in diameter which can be hardened through satisfactorily and without much warpage, it is possible to employ carbon steels with improving heat treatment (hardening + tempering at 500-550°C).

Among the inexpensive alloying elements, such as manganese, silicon, and chromium, the latter should be preferred. A steel alloyed with 1% Cr (compare steel Grades 40 and 40X) can be hardened through by oil quenching in sections up to 20 mm in diameter with a slight decrease in the ductile-to-brittle transition temperature (most probably, owing to grain refinement produced by the addition of chromium); on the contrary, manganese and silicon in most cases raise the ductile-to-brittle transition temperature.

For that reason, the mechanical properties of simple alloyed steels of the 40X type usually are quite satisfactory for making machine parts of small cross-section. An addition of boron ($\approx 0.003\%$) increases the maximum diameter of parts which can be made from the steel, but raises somewhat the ductile-to-brittle transition temperature, though the margin of toughness will be not less than in carbon steels.

Alloying of chromium steels with other elements also improves the hardenability. Parts 20 to 40 mm in diameter can be made of other steels of group III, as well as of steel Grade 40XP. Steels of that group are additionally alloyed with manganese, molybdenum, silicon, and titanium. All these elements increase the hardenability and all of them, except for molybdenum, diminish the margin of toughness. Steel Grade 30XM may be distinguished in this group by its high toughness. Though the hardenability of that steel is only slightly higher than that of steel Grade 40X, its ductile-to-brittle transition temperature is substantially lower; besides, steel Grade 30XM is (as other molybdenum steels) insensitive to second-order temper brittleness.

The next group are nickel steels with 1-1.5% Ni. As has been noted earlier, nickel differs from other elements in that it can improve the hardenability

[1] The final structure is formed through air cooling after rolling.

Table 16.6. Compositions of Improvable Structural Steels (GOST 4543—71)

Group	Steel Grade	Content of elements, %						Critical diameter, mm	Ductile-to-brittle transition temperature, °C
		C	Mn	Si	Cr	Ni	Other elements		
I	40	0.37-0.44	—	—	—	—	—	10	—20
	45	0.42-0.49	—	—	—	—	—	12	—20
II	40X	0.36-0.44	—	—	0.8-1.1	—	—	15	—50
	40XP	0.37-0.45	—	—	0.8-1.1	—	0.002-0.005 B	20	—30
III	30XM	0.26-0.34	—	—	0.8-1.1	—	0.15-0.25 Mo	20	—60
	40XΓ	0.36-0.45	0.9-1.2	—	0.9-1.2	—	—	25	—20
	40XΓP	0.37-0.45	0.7-1.0	—	0.8 1.1	—	0.002-0.005 B	30	—20
	30XΓT	0.24-0.32	0.8-1.1	—	1.0-1.3	—	0.06-0.12 Ti	20	—20
	30XΓC	0.28-0.35	0.8-1.1	0.9-1.2	0.8-1.1	—	—	25	—20

IV	40XH	0.36-0.44	—	0.17-0.37	0.45-0.75	1.0-1.4	—	25	—60
	40XHP	0.35-0.42	0.6-0.9	0.17-0.37	0.6-0.9	0.4-0.8	0.002-0.005 B	35	—40
	40XΓHP	0.35-0.45	0.8-1.1	0.17-0.37	0.8-1.1	0.5-0.8	0.002-0.005 B	40	—20
	40XHM	0.37-0.44	—	0.17-0.37	0.6-0.9	1.2-1.6	0.15-0.25 Mo	40	—80
	42XMΦ	0.40-0.45	0.5-0.8	0.17-0.37	0.8-1.1	—	0.20-0.30 Mo, 0.08-0.14 V	40	—60
V	30XH3	0.27-0.34	—	—	0.6-1.9	2.75-3.15	—	50	—100
	30XH2BΦ	0.27-0.34	—	—	0.6-0.9	2.0-2.4	0.5-0.8 W, 0.15-0.30 V	100	—80
	38XH3MΦ	0.30-0.42	—	—	1.2-1.5	3.0-3.4	0.35-0.45 Mo, 0.1-0.2 V	100	—100

Notes: 1. With the usual content of manganese and silicon (0.4-0.8% Mn and 0.15-0.40% Si), their presence is not indicated.

2. The allowable content of occasional impurities (including those which serve as alloying elements in other steels) is not specified.

3. Most of these steels are manufactured with a common (approx. 0.035%) or reduced ($\leqslant 0.030$ or 0.025%) content of sulphur and phosphorus; in the latter case, a letter A is written at the end of grading.

4. The critical diameter is given for full hardenability of 95% of martensite at the lower content of carbon and alloying elements and for oil quenching (or for water quenching for Group-I steels).

5. The ductile-to-brittle transition temperature is the temperature at which a steel in improved state (at $\sigma_t = 100$ kgf/mm^2) has 50% of fibres in the fracture; it is determined by impact tests of notched ($r = 1$ mm) specimens 10×10 mm in cross-section (through hardened in all cases).

6. Steel Grades 40XHP, 40XΓHP and 42XMΦA are not covered by the USSR Standard (GOST) 4543—71.

and at the same time lower the ductile-to-brittle transition temperature. Steels of group IV can be recommended for making machine parts up to 40-70 mm in diameter.

Comparing steel Grades 40XH, 40XHP and 40XГHP, it may be seen that an addition of boron and manganese improves the hardenability and at the same time lowers the margin of toughness. Steel Grade 40XHM is the best in this group as regards the hardenability and margin of toughness, which may be explained by the effect of complex alloying (Cr + Ni + Mo) and a higher content in nickel than in other steels of the group.

Parts more than 70 mm in diameter, when through hardening is needed, should be made of steels with 2-3% Ni. The commonest steels of this type are included in group V. It is not practicable to use for the purpose purely chromium-nickel steels, such as Grade 30XH3, which were earlier employed quite expensively. The point is that these steels are very susceptible to second-order temper brittleness. Therefore, large-size steel elements to be subjected to high dynamic loads should be preferably made of Cr-Ni-Mo or Cr-Ni-Mo-V steels. Owing to the high content in nickel, the ductile-to-brittle transition temperature of these steels is lower than in other steels.

The level of mechanical properties can be varied within wide limits depending on the conditions of heat treatment, mainly on the temperature of tempering. With almost all steel grades given in Table 16.3, the properties indicated in Table 16.1 can be obtained (under provision of through hardening) by varying the temperature of tempering.

The mixture of martensitic, bainitic and pearlitic structures which is really formed in these steels owing to their different hardenability over the cross-section can produce a rather variegated pattern of properties. For every point of the cross-section, however, the mechanical properties (upon tempering) cannot differ appreciably from those given in Table 16.1.

We now analyse the mechanical properties of some most popular grades of improvable steels.

Figure 16.12*a* shows the mechanical properties of carbon steel Grade 40. The curves in the left-hand portion of the figure represent the properties of the steel in specimens 3-5 mm in diameter as a function of the tempering temperature (the time of tempering was 1 h). The right-hand portion gives the properties of the steel in the core depending on the part diameter (t_{temp} = 580°C).

The tempering temperature *versus* property curves show the typical variations of steel properties with tempering temperature. In particular, the strength diminishes and the ductility and toughness increase with increasing temperature of tempering. The minimum of impact toughness is observed at 250°C, when first-order temper brittleness appears in the steel.

Tempering within a range of 200-600°C can vary the mechanical properties quite widely:

t_{temp}, °C	200	600
σ_t, kgf/mm²	180	60
ψ, %	30	60
a_{nI}, kgf m/cm²	2	16
T_{50}, °C	20	—20

These values can be obtained in carbon steel only in parts up to 10-15 mm in diameter (see the right-hand diagram in Fig. 16.12*a*).

Upon tempering at 580°C in parts of various cross-section, the following values can be obtained (at $\sigma_t \approx 70$ kgf/mm²):

cross-sectional diameter, mm	15	30
a_{nI}, kgf m/cm²	14	8
ψ, %	60	45
$\sigma_{0.2}$, kgf/mm²	50	40

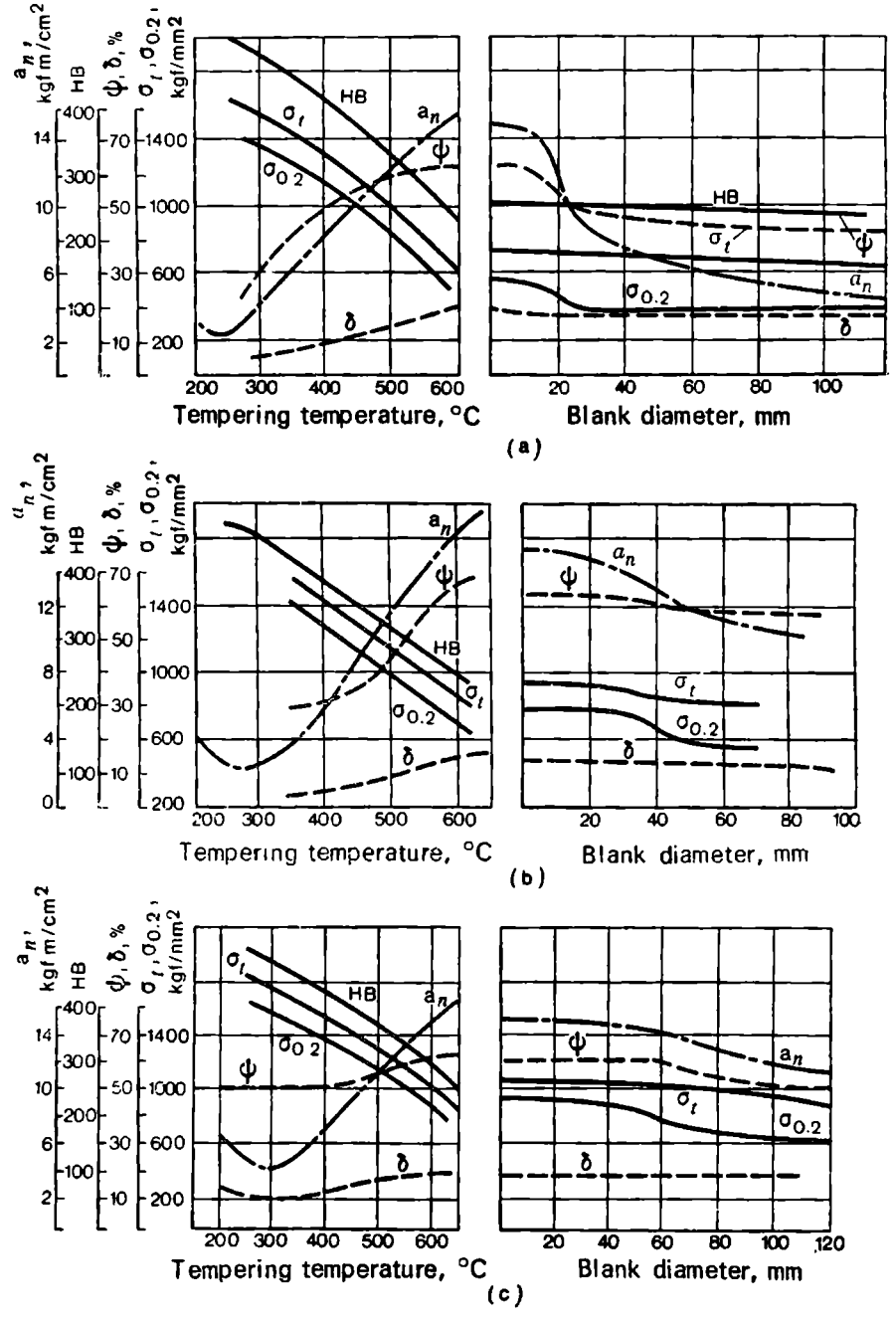


Fig. 16.12. Effect of tempering temperature and the mass of blank on the mechanical properties of various steels

(*a*) steel 40; (*b*) 40X; (*c*) 40XHM

In sections over 30 mm in diameter, the properties vary only insignificantly (except for a_{nI}).

The properties in the core[1] of a rod 30 mm in diameter correspond to the property values given in Table 16.1 (i.e. the properties of the products of direct decomposition of austenite, but not of martensite).

If it is required to have a high strength and high values of ductility and toughness in large-size parts, these should be made of an alloy steel that can be hardened to an appreciable depth, such as Grades 40X and 40XHM. The mechanical properties of these steels as a function of the temperature of tempering and the cross-section are shown in Fig. 16.12*b* and *c*.

The pattern of variation of mechanical properties depending on tempering temperature is similar for all the three steels discussed and, for the same level of strength, other properties of all these steels are very close. Owing, however, to a different hardenability, the property *versus* size patterns of the curves for a heat-treated part are different. The high mechanical properties upon heat treatment can be obtained in sections up to 20-25 mm in diameter for steel 40X and up to 50-60 mm for steel 40XHM (in both instances upon oil quenching), i.e. in appreciably larger sections than is possible with steel 40.

With more heavily alloyed steels, the properties are worsened less intensively with increasing diameter of a heat-treated part.

The rules for selecting a steel grade may be briefly formulated as follows: (a) the selection of a steel grade (degree of alloying) is determined by the size of a heat-treated part; (b) the level of strength determines the temperature of tempering; (c) the presence of stress concentrators and dynamic loads determines the necessity of alloying with elements which can lower the ductile-to-brittle transition temperature (nickel) or calls for the use of a steel of elevated or high purity.

[1] The lower values in the core are also associated with the fact that the core contains the highest amounts of impurities (sulphur and phosphorus) which lower the ductility.

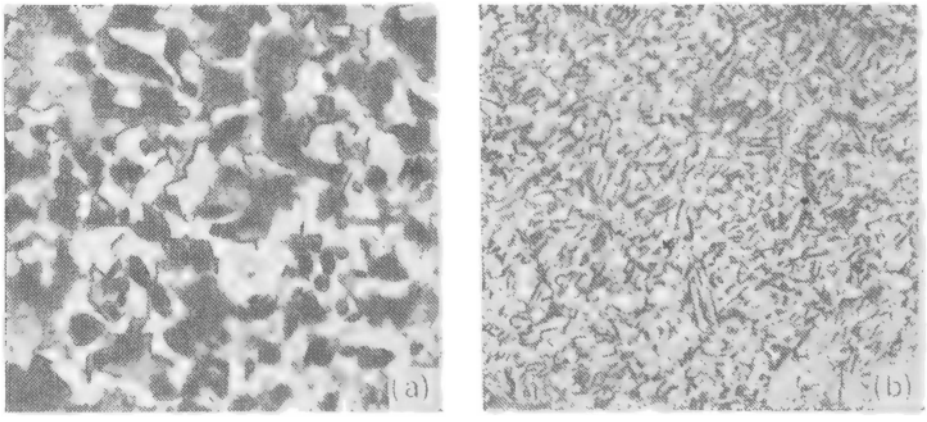


Fig. 16.13. Microstructure of steel 30ХГСА. ×500

(*a*) as annealed; (*b*) as improved

All medium-carbon structural alloy steels have roughly the same structure upon annealing, which consists of ferrite and pearlite[1]. The structure of a heat treated steel is formed of the products of martensitic breakdown. The improvement of the mechanical properties of steel upon two-stage heat treatment is only observed on tempering at a temperature at which the martensitic orientation is retained. The typical structures of improvable structural steels are shown in Fig. 16.13*a* and *b*.

16.5. HIGH-STRENGTH STEELS

The structural steels described in the two previous sections are heat treated to have a strength (σ_t) up to 120-140 kgf/mm^2 and the structure of temper martensite (low-carbon steels) or sorbite (medium-carbon steels).

With such a structure and strength, a steel possesses a high ductility and high toughness and can be employed in elements of intricate shape and subjected to dynamic and fatigue loads.

Modern engineering, however, sets forth ever increasing requirements to strength; in certain applications, materials having a strength of 180-200 kgf/mm^2 or even more are needed, with the operating conditions and the shape of parts allowing a lower ductility and lower toughness compared with common improvable steels. A high strength is achieved by properly selecting the steel composition and the specific conditions of heat treatment. These steels, which are heat treated to a high strength ($\sigma_t > 150$ kgf/mm^2) are called *high-strength* steels.

With common heat treatment (hardening + tempering), the strength is determined by carbon content and tempering temperature. The strength of steel decreases with increasing temperature of tempering (Fig. 16.12). As may be seen from Fig. 16.12, the strength obtained after tempering at 200°C[2] is as high as 180 kgf/mm^2, i.e. common medium-carbon steels (0.3-0.4% C), when hardened and tempered at a low temperature, can have a strength of 170-200 kgf/mm^2 (see Fig. 16.12). Carbon can, however, increase the strength only to a definite limit (0.4%), so that no gain in strength is obtained at higher concentrations of carbon and the value of σ_t becomes unstable (Fig. 16.14). This can be explained by the fact that a simple increase in carbon content results in a higher ductile-to-brittle transition temperature and at σ_t above 200 kgf/mm^2 almost fully brittle fracture takes place.

[1] The quantity of pearlite is higher at a higher content of carbon and alloying elements, since most of the alloying elements shift the *S* point to the left, see Fig. 15.1.

[2] Tempering at 200°C gives the highest strength.

This is why such high-strength steels, i.e. common steels with 0.3-0.4% C, but tempered at a low temperature, are employed relatively seldom. They can be only employed in parts not to be subjected to dynamic loads and having no stress concentrators.

Practically, common steels are only rarely treated by common methods to a strength above 150 kgf/mm² [1].

Nevertheless, modern engineering is in demand for materials (steel) with $\sigma_t > 150$ kgf/mm². Some methods have also been developed for ensuring an adequate toughness at the strength values above 150 kgf/mm².

The principal ways for obtaining a high strength (more strictly, an adequate toughness at a high strength) have been discussed earlier (see Sec. 16.1). Consider the particular strengthening methods employed.

Alloying elements, and especially carbide-forming ones, retard the processes of softening during tempering. If a structural steel with a common carbon content (at 0.3%) has an elevated content of carbide-forming elements (chromium, molybdenum, tungsten, vanadium), its hardness will be retained up to quite high temperatures of tempering (500-550°C, see Fig. 16.15). If the steel is now tempered at 500°C, instead of being tempered for the maximum strength at 200°C, hardening stresses in it will be eliminated to a large extent and we can expect a higher toughness.

An example may be steel Grade 30Х5МСФА, which contains 0.3% C, 5% Cr, 1% Mo, 1% Si, and 0.5% V. Its mechanical properties upon hardening from 1 000°C and tempering at 500°C are as follows: $\sigma_t = 180$ kgf/mm², $\sigma_{0.2} = 160$ kgf/mm², $\psi = 45\%$, $a = 5$ kgfm/cm², $B = 40\%$ [2] (the values relate to vacuum-melted metal)

Lowering of the ductile-to-brittle transition temperature and an increase of the percentage of fibres in the fracture result in better mechanical properties. The most simple solution of the problem is alloying with nickel, an element that lowers the ductile-to-brittle transition point, and therefore, increases the percentage of fibres in the fracture of high-strength steels. This improves the toughness of a steel, but in common steels the content of nickel cannot be increased above 4 per cent because of the appearance of retained austenite (which has a reduced strength and the products of its decomposition, a reduced toughness). This lowers the Ac_1 point so that high-temperature tempering becomes impossible. The problem of application of high-nickel steels has been solved by complex alloying of steel with nickel and cobalt. Cobalt raises the martensitic point (Fig. 16.16)

[1] This is only an approximate limit.

[2] B is the percentage of ductile fibres in a fracture.

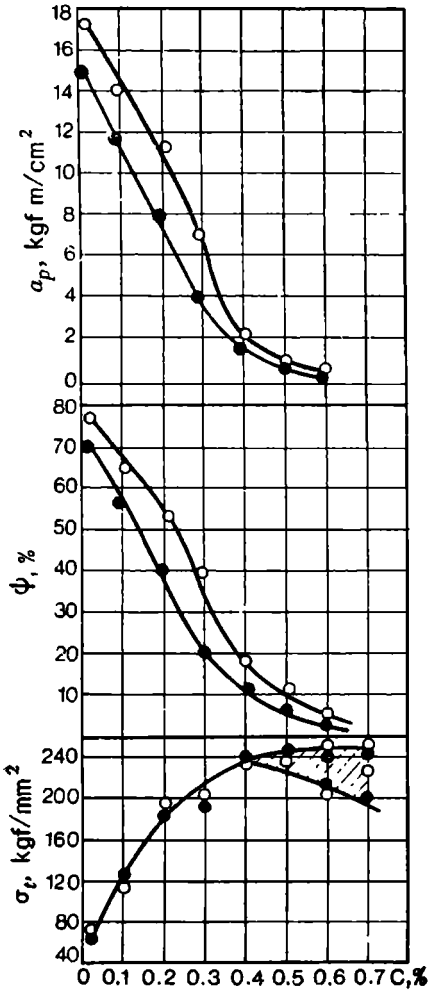


Fig. 16.14. Effect of carbon on the ultimate strength (σ_t), ductility (ψ) and the work of crack propagation (a_p)

black dots — upon conventional heat treatment; white dots — upon HTHT. Steel type X5M2CΦ (the author)

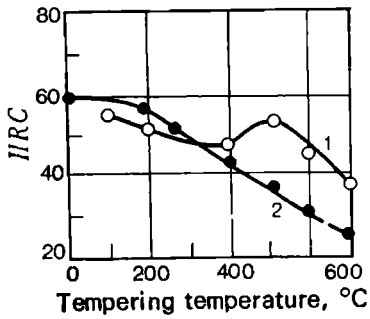


Fig. 16.15. Effect of tempering temperature on hardness

1 — steel 30X5M2CΦ; *2* —40XHM

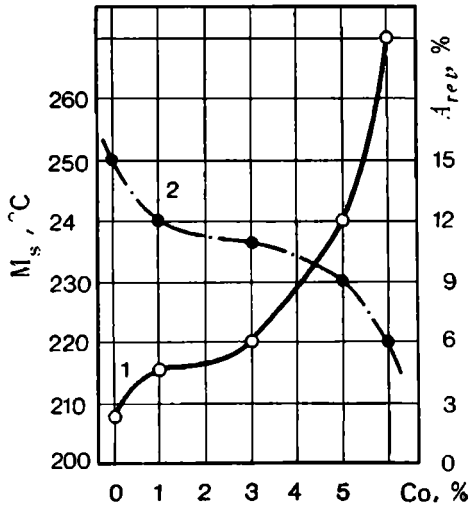


Fig. 16.16. Effect of cobalt on (*1*) martensitic point and (*2*) quantity of retained austenite in steel with 0.3% C and 9% Ni (the author)

and thus diminishes the content of retained austenite. On the other hand, it raises the Ac_1 point and enables high-temperature tempering.

Take as an example a steel with 0.3% C 9% Ni, and 4% Co, which after common heat treatment (hardening + tempering at 200°C) has a high strength (σ_t = 160 kgf/mm²) and a high complex of ductility and toughness (ψ = 60%, T_{50} = −110°C, and a_p^{20} = 2.5 kgf m/cm²); in this respect it is equivalent to steel Grade 18X2H4BA, but at strength σ_t = 130 kgf/mm².

Another method for increasing the toughness, i.e. lowering the ductile-to-brittle transition point, is refinement of steel grain to

fine (No. 8-10) or extra-fine (No. 11-13) size. As has been noted earlier, refinement of grain results in a lower ductile-to-brittle transition point, and therefore, a higher percentage of fibres in the fracture. Grain refinement can be obtained by using high heating rates or by high-temperature thermomechanical treatment (HTHT); in this process, hardening fixes the state when the primary recrystallization has come to an end, but grain growth has not yet started.

Figure 16.14 shows the effect of carbon on the properties of steel type X5MCΦA upon common heat treatment and high-temperature thermomechanical treatment. In the former case, the grain size is No. 4 or 5 and in the latter, No. 8. As may be seen, high-temperature thermomechanical treatment has not affected the strength, but increased appreciably the ductility (ψ) and the resistance to brittle fracture (T_{50}).

Using high-temperature thermomechanical treatment with clean vacuum-melted steel (for instance, Grade 30X5M2CΦA), it is possible, for the same strength (σ_t = 220 kgf/mm²), to obtain the mechanical properties as follows: $\sigma_{0.2}$ = 180 kgf/mm², ψ = 40 per cent, a_n = 5 kgf m/cm², B = 50 per cent, a_p = 6 kgf m/cm², and a_p^{20} = 3 kgf m/cm².

The advantages of high-temperature thermomechanical treatment have been confirmed by determining the toughness properties by the methods of linear mechanics (K. Mazanets et al., Table 16.7). Note that this advantage becomes

Table 16.7. Fracture Toughness of High-strength Steel

C, %	Type of heat treatment	Tempering temperature, °C	σ_t, kgf/mm²	G_{I_c}, kgf/mm²	K_{I_c}, kgf/mm$^{3/2}$
0.25	Common heat treatment	200	137	64	367
	High-temperature thermomechanical treatment	200	145	64	367
0.41	Common heat treatment	100	231	10	148
	High-temperature thermomechanical treatment	200	216	20	205
0.48	Common heat treatment	200	216	9	124
	High-temperature thermomechanical treatment	200	232	11	167

noticeable only upon treatment to a high strength (above 150 kgf/mm²), when evidently there appears a difference in the type of fracture. At $\sigma_t < 150$ kgf/mm², the ductile-to-brittle transition point is below the room temperature and the fracture is ductile in both cases (common heat treatment and high-temperature thermomechanical treatment; at $\sigma_t > 200$ kgf/mm², the fracture is semi-brittle

in both cases, but with a lower percentage of fibres in the steel upon common heat treatment.

High-temperature thermomechanical treatment, which provides a high complex of mechanical properties in steel, has been studied quite thoroughly, though is not employed as widely as it deserves.

Other methods for grain refinement (alloying of high-strength steel with nitrides, high-speed heating, etc.) are still being studied.

Steels having the structure of medium-carbon martensite can also be strengthened by a slight plastic deformation upon heat treatment. The method usually does not change the strength (σ_t), but increases the yield limit practically to the value of ultimate strength (upon thermomechanical treatment, the yield limit obtained is usually appreciably lower numerically than the ultimate strength, though in most cases it is more important to raise the yield limit, rather than the ultimate strength).

In the cases considered, the strengthening effect (high dislocation density) is obtained through martensitic transformation. The martensite that forms in carbon-containing steels has a fine-block structure and appreciable second-order internal stresses. At lower concentrations of carbon, the width of blurring of the lines in radiograms becomes narrower (owing to a lower dislocation density in the martensite) and at very low concentrations of carbon (say, 0.03%), the strength of martensite (acicular ferrite) does not exceed 100-120 kgf/mm^2. If however this ferrite (martensite) contains elements which can form intermetallic phases, it is possible to strengthen the metal by a secondary process of precipitation hardening associated with precipitation (separation) of intermetallic phases.

Steels capable of undergoing intermetallic strengthening have been developed recently. They are called *martensite-ageing*, or *maraging*, steels. Upon hardening, they form practically carbonless martensite and on subsequent tempering (approximately at 500°C), intermetallic phases precipitate in them. The mechanical properties thus obtained are as follows: $\sigma_t = 180$ kgf/mm^2, $\sigma_{0.2} = 150$ kgf/mm^2, $\delta = 12$ per cent, $\psi = 40$ per cent, and $a_n = 6$-10 kgf m/cm^2.

Maraging steels usually contain 18% Ni and are additionally alloyed with titanium and aluminium and often also with cobalt and molybdenum. Some compositions may have a lower (8-10%) or a larger (up to 25%) content of nickel.

The alloying with nickel and titanium is needed to form intermetallic phases of the type of NiTi or Ni_3Ti (titanium can be partially replaced by aluminium) which cause ageing. The content of carbon should be as low as possible ($< 0.03\%$), otherwise carbides will form in place of intermetallic phases and impair the effect of precipitation hardening.

In view of the high content in alloying elements and low content in carbon, maraging steels can be quenched on hardening at any

high rate without danger of forming non-martensitic products o austenitic transformation. In the most popular maraging steel (with $<$ 0.03% C, 18% Ni, 10% Co, 5% Mo, 0.5% Ti, and 0.1% Al), the martensitic transformation begins at 150-200°C and is practically completed (less than 10% of retained austenite) at room temperature. At a content of nickel above 18 per cent, the martensitic transformation is completed at sub-zero temperatures, i.e. the steel requires sub-zero treatment, which however ensures better properties (to be discussed later).

The martensite formed on 'hardening' has a low strength and very high ductility. A steel in this 'hardened' state can be plastic worked, machined or processed in other technological operations.

The final strength properties are formed upon subsequent (after deforming) tempering (ageing) at 480-500°C.

The mechanical properties of maraging steels with 18% Ni are typically as follows: σ_t = 180 kgf/mm^2, δ = 15 per cent, ψ = = 65 per cent; those of steels with 25% Ni: σ_t = 220 kgf/mm^2, δ = = 12 per cent, and ψ = 55 per cent.

With such a high content of nickel, fracture is ductile at any strength level and any temperature, though the value of a_p diminishes with increasing ultimate strength and is only 1 kgf m/cm^2 at σ_t = 240 kgf/mm^2.

The composition of selected maraging steels is given in Table 16.8.

Table 16.8. Composition and Mechanical Properties of Maraging Steels

Steel Grade	Content of main elements, %				Principal mechanical properties			
	Ni	Co	Mo	Ti	σ_0	ψ	a_n	a_p
H18K8M3	18	8	3	0.2	140	65	8	3.6
H18K8M5T	18	8	5	0.5	180	60	5	2
H18K12M5T	18	12	5	1.5	240	30	2	0.5

Note. The steels indicated also contain 0.03% C, 0.05-0.15% Al, 0.01% S, and 0.01% P.

Another class of high-strength steels of elevated plasticity, called *TRIP-steels*[1], has been developed quite recently. A favourable combination of a high strength and high plasticity is obtained in them by properly selecting their composition and the conditions of heat treatment and temperature deformation.

[1] An abbreviation for 'Transformation induced plasticity'.

The composition of the steel should be such that the hardening (from 1 000-1 100°C) could fix a purely austenitic structure at room temperature (i.e. points M_s and M_D should be below 0°C*). After that, the steel is deformed at a temperature not exceeding the recrystallization point (i.e. below 600°C).

The austenitic state remains in the metal on cooling to room temperature, with point M_s still lying below room temperature, but point M_D has already shifted into the zone of positive temperatures owing to depletion of the austenite in carbon and alloying elements. Deformation at room-temperature tests results in the formation of martensite. Thus, the original austenitic state, which is strengthened relatively weakly, changes to the high-strength martensitic state upon testing (or in operation).

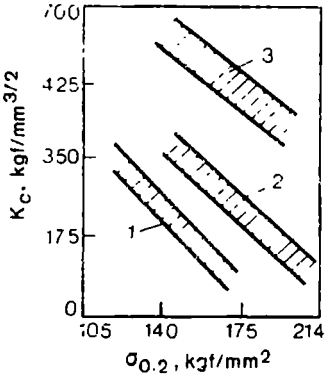


Fig. 16.17. Fracture toughness of high-strength steels

1 — steel 30ХН3М; *2* — maraging steel; *3* — TRIP-steel

The typical composition of TRIP-steels is as follows: 0.3% C, 9% Cr, 8% Ni, 4% Mo, 2% Mn, and 2% Si or 0.25% C, 25% Ni, 4% Mo, and 1.5% Mn. There are also other grades of TRIP-steel which are alloyed heavily to produce the TRIP-effect (i.e. to have the M_s and M_D points below room temperature in as-hardened state, but M_s point below and M_D point above room temperature after work-hardening). Deforming for work-hardening (with a high deformation of 60 to 80%) is carried out at a temperature of 400-500°C.

The mechanical properties of TRIP-steels are, typically as follows: $\sigma_{0.2}$ = 140-170 kgf/mm^2, σ_t = 180-200 kgf/mm^2, and δ = = 20-30 per cent.

An especially favourable property of these steels is a high resistance to crack propagation. For instance, the fracture toughness (the stress intensity at the tip of crack, K_c) at $\sigma_{0.2}$ = 150 kgf/mm^2 is 175 kgf/mm$^{3/2}$ for common Cr-Ni-Mo steel, about 300 kgf/mm$^{3/2}$ for a maraging steel of comparable strength, and more than 500 kgf/mm$^{3/2}$ for a TRIP-steel (Fig. 16.17).

At present, TRIP-steels seem to have the best combination of strength and toughness, i.e. to be the most reliable structural material.

Tests of mechanical properties of steels have shown that their plastic and ductile properties, and therefore, the ability to be strengthened, depend on purity, i.e. the content of interstitial impurities (nitrogen, oxygen, hydrogen) and non-metallic inclusions. Interstitial impurities, i.e. the elements that can form interstitial solid

* M_D is the temperature above which deformation cannot cause martensitic transformation.

solutions with iron, produce local distortions of the lattice and inhibit dislocation movement. This impedes plastic deformation and facilitates crack initiation at tangles of sessile dislocations.

Non-metallic inclusions (nitrides, oxides, sulphides) are stretched in the direction of rolling and thus become places of stress concentrations, which have an especially marked effect in the transverse properties of metal, i.e. the properties of specimens cut across the direction of rolling. This is why the use of high-purity alloys is one of the most effective methods for increasing the strength (more accurately, the plasticity and toughness).

The recent progress in practical metallurgy has provided conditions for the manufacture of metals of higher purity, and therefore, greater reliability.

The treatment of open-hearth metal with synthetic slags (prepared in a separate furnace) is effective for lowering the content of oxygen and sulphur in steel, and therefore, diminishing the content of oxides and sulphides; this sharply increases the toughness of metal in cross-cut specimens.

A lower content of gases in steel can be obtained by vacuum melting and vacuum degassing.

Let us consider some examples. Compare steel type 40ХГСНМФ from two melts of a very close analysis, but made by various processes. The steel made at atmospheric pressure had 250 at. ppm oxygen and 50 at. ppm hydrogen, and that made by vacuum melting, respectively 75 and 20 at. ppm. The values of σ_t and $\sigma_{0.2}$ in the two melts were almost the same, but ψ and σ_{-1} differed markedly (Table 16.9).

Table 16.9. Comparison of the Properties of Steel Grade 40ХГСНМФ Melted at Atmospheric Pressure (Numerators) and in Vacuum (Denominators)

σ_t, kgf/mm²	ψ, %	σ_{-1}, kgf/mm²	σ_t, kgf/mm²	ψ, %	σ_{-1}, kgf/mm²
100	30/55	55/55	180	20,30	75/88
140	25/40	76/77	200	15/25	62/90

Though the strength of steel attained in some laboratory experiments is as high as $\sigma_t = 300$ kgf/mm², it is only one-fourth of the theoretical value. The possibilities for making high-strength materials (more strictly, material + + strengthening process) are far from being exhausted. By some forecasts, future industrial iron-base alloys will have $\sigma_{0.2} = 280$ kgf/mm² and $\sigma_t = 320$ kgf/mm².

16.6. WELDABILITY OF STEEL

Welding is now used extensively in residential and industrial construction, construction of bridges, gas and oil pipelines and in many branches of engineering technology. Most steel elements, ex-

cept for moving machine parts, are, as a rule, welded together. This is why the weldability of steel is the property of prime importance. In the earlier sections we have considered structural (cementable and improvable) and high-strength steels with which welding is used not as frequently as with constructional steels. For that reason, before dealing with constructional steels, it is reasonable to discuss briefly what determines a good weldability of steel.

Welded joints should be dense and of the same strength as the parent metal. The principal type of welding is by fusion in which metal is fused in a joint and heats up the adjacent portions of the parent metal. Three zones may be distinguished in a weld joint (Fig. 16.18); weld metal *I* (cast structure); heat-affected zone *II* which is heated up above the critical point during welding; and zone *III* which is heated up to a temperature below the critical point.

The integrity, and therefore the strength of weld joints is mainly affected by cracks which can appear owing to a high temperature gradient in the weld and to the associated internal stresses.

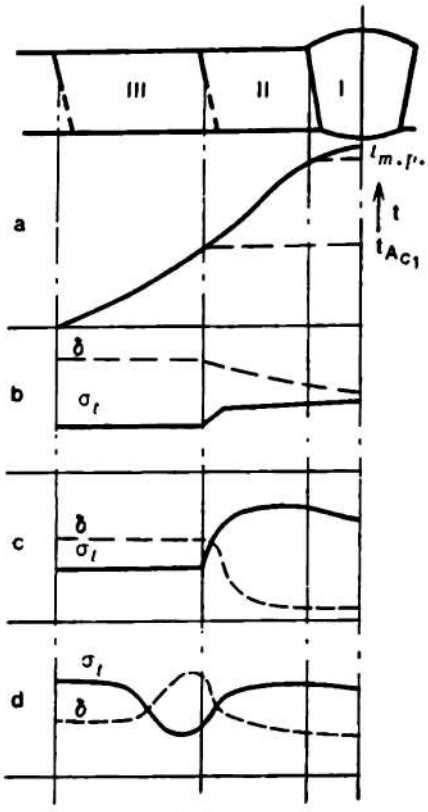
Welding cracks may be either hot or cold. The former appear mainly in the weld proper during solidification, i.e. when the metal is still semi-solid (crystals + liquid) and has a low strength. Given equal conditions, the danger of hot cracking is more probable if the weld metal is for a long time in that state. The elements which widen the interval between the liquidus and solidus lines increase the susceptibility to hot cracking. In this respect, carbon has an unfavourable effect, since it widens the interval of solidification and thus promotes hot cracking.

Cold cracks may appear owing to martensitic transformation. This is why cold cracking is promoted by the alloying elements which can cause undercooling of the austenite to the temperature of martensitic transformation in zones heated above the critical point. Carbon increases the volumetric effect of martensitic transformation and thus makes a steel more susceptible to cold cracking.

In view of the foregoing, the content of carbon in welded steels is usually limited at 0.22-0.25 per cent. It should be even lower in more intensive welding methods associated with large temperature changes or high welding stresses.

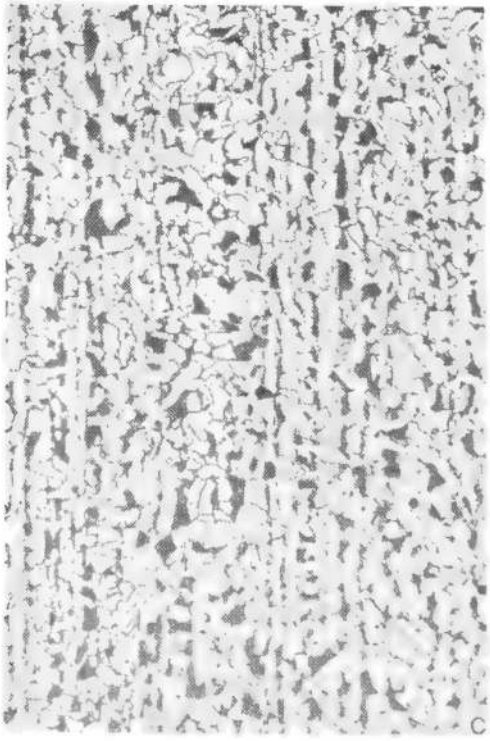
The weld metal differs from the parent metal in the composition, as well as in the structure (cast structure in the weld and deformed structure in parent metal). The effect of the cast structure of weld, which is unfavourable for the strength, can be weakened or eliminated by properly selecting the composition of electrode wires and that of electrode covering.

With these real methods for controlling the strength of weld metal it may be taken generally that the weld metal has the same strength as the parent metal. Things are different with the heat-affected

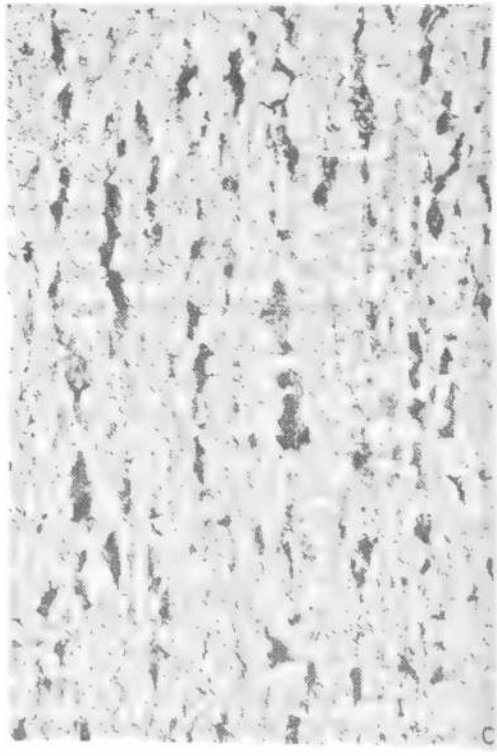


(a)

(b)



(c)



(d)

Fig. 16.18. Variations of temperature and mechanical properties in weld zone (*a*) and the structure of low-alloy steel in hot rolled state (*b*), normalized state (*c*), upon controlled rolling (*d*)

a — temperature distribution; *b-d* — mechanical properties; (*b* — low-carbon unalloyed steel; *c* — alloy steel; *d* — heat-strengthened steel)

zone. Its composition does not change on welding, but the structure changes and not in a good sense. Thus, the response of the parent metal to the thermal conditions of welding is what characterizes in the first place the weldability of steel.

When the original annealed metal is heated below Ac_1, no marked changes occur in its properties, i.e. no changes in zone *III* (Fig. 16.18). On the other hand, zone *II* will be heated above the critical point and two extreme cases are possible here:

1. A low-carbon low-alloy steel, a wide zone of thermal influence (high energy of welding), and slow cooling upon welding. In that case, zone *II* will restore its original pearlite-ferritic structure with a slightly coarsened grain and will have a somewhat lower plasticity (Fig. 16.18*b*).

2. An alloy steel (in which the austenite is prone to undercooling), a narrow thermal influence zone, and fast cooling upon welding. This causes grain growth of austenite and appreciably coarser structure upon welding. The strength of metal in the zone increases, but the plasticity drops down abruptly, often to zero (Fig. 16.18*c*).

The latter extreme case should be avoided. Practically, zone *II* in low-alloy steels undergoes strengthening on welding and loses much in its plasticity.

If a steel is welded after having been strengthened thermally, the structural changes will also affect zone *III* (Fig. 16.18*d*). The metal here will be tempered almost to the as-annealed state (fully annealed in a narrow band). The depth of softening is determined by the steel composition (in particular, by the liability to softening on tempering) and the width, by the welding conditions.

By properly selecting the steel composition (alloying with elements which can retard the softening, such as silicon, molybdenum or vanadium) and welding conditions, it is possible to diminish the depth and width of the softened zone, but the zone will form inevitably and this should be considered when estimating the strength of welded joints.

In plain carbon steels, the strength in the zone of maximum softening of the parent metal decreases to 50-60 kgf/mm^2, irrespective of the original strength value. In steels specially alloyed with the elements mentioned above, the strength in the softening zone remains at a level of 80-90 kgf/mm^2.

16.7. CONSTRUCTIONAL STEEL

Constructional steels are used for manufacturing building structures: bridges, oil and gas pipelines, frameworks, boilers, etc. All building structures are made predominantly by welding, so that the weldability of constructional steel is one of the most important characteristics. As has been given earlier, constructional steels be-

long to the class of low-carbon steels with C < 0.22-0.25 per cent. An elevated strength is usually ensured by alloying with less expensive elements: manganese and silicon. At a low content of carbon, alloying can increase the yield limit up to 40-45 kgf mm^2 (and the ultimate strength, up to 50-60 kgf mm^2), or even higher if the steel is heat treated.

Plain carbon constructional steels are specified by the State Standard GOST 380-71 as Grades Ст1, Ст2, Ст3. Among them, Ст3 is most popular. It should satisfy the specification of group B (carbon content below 0.22% and σ_y equal to 24 kgf/mm^2) when used in welded structures and satisfy the specification of group A (with only σ_y not less than 24 kgf mm^2 being guaranteed) when used in non-welded structures. Killed steel is more reliable, as having a lower ductile-to-brittle transition temperature, than semi-killed or rimming steel, as may be seen from the following:

Steel	T_{50},°C
Killed	0
Semi-killed	10
Rimming	20

This relates to hot-rolled steel. Normalizing cannot affect the strength characteristics[1], but refines the ferrite-pearlitic structure and lowers the ductile-to-brittle transition point due to recrystallization.

Thermal improvement (hardening + tempering at 600-650°C) can produce a greater effect: increase somewhat the yield limit (σ_y > 28-30 kgf mm^2) and lower appreciably the ductile-to-brittle point:

Ст3сп	T_{50},°C
Hot-rolled	0
Normalized	−20
Improved	−40

Thus, it is advisable to use rimming steel in non-welded (and less-critical welded) structures and semi-killed or killed steel, in critical welded structures. Normalized or thermally improved steel should be used in most critical structures and for operation at low temperatures (—40 to —60°C)[2].

Since the strength characteristics of Ст3 cannot be increased appreciably by heat treatment (hardening + tempering at 600°C)[3], alloy steels are used in place of it when a higher yield limit is essential. These are usually called *low-alloy*, or *constructional*, steels of elevated strength. In contrast to structural alloy steels, they are not heat treated at the consumer, i.e. their structure and service properties are formed during the manufacture.

The compositions of the most popular grades of this type of steel are given in Table 16.10.

All the steels given in the table are intended for use in welded structures (in the first place in large gas pipelines up to 1 220-1 420 mm in diameter) and have a low content of carbon and other alloying el ments.

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[1] Since the cooling conditions after normalizing are roughly the same as after rolling.

[2] Our recommendations are only approximate, since T_{50} may be largely dependent on grain size, purity and other factors.

[3] The strength naturally will be higher on tempering at temperatures below 600-650°C, but this cannot ensure a high plasticity and the strengthening effect will be lost on welding.

Table 16.10. Compositions and Mechanical Properties of Constructional Low-alloy Steels

Nos.	Steel group	Steel Grade	Composition, %						Mechanical properties				
			C	Si	Mn	Nb	V	N	σ_t, kgf/mm²	σ_y, kgf/mm²	δ, %	$a^{-40}_{0.25}$, kgf m/cm²	T_{50}, °C
1	Hot-rolled carbon steels	Ст3	0.2	0.2	0.5	—	—	—	45	25	30	1	0
2		Ст3пс	0.2	0.1	0.5	—	—	—	45	25	30	0.5	+10
3		Ст3кп	0.2	0.05	0.5	—	—	—	45	25	30	0.5	+40
4	Hot-rolled low-alloy steel	17ГС	0.2	0.6	1.4	—	—	—	50	35	25	2	—10
5	Normalized low-alloy steels	17Г1С	0.2	0.6	1.6	—	—	—	52	36	25	4	—30
6		17Г1Су[1]	0.2	0.6	1.6	—	—	—	52	36	23	5	—20
7		14Г2САФ	0.18	0.5	1.6	—	0.12	0.03	57	40	25	7	—40
8		17Г2СФБ	0.18	0.5	1.6	0.04	0.08	0.02	60	42	25	7	—50
9	Low-alloy steels, controlled rolling	07Г2ФБ	0.10	0.4	1.7	0.05	0.08	0.02	57	4[illegible]	25	8	—60
10		08Г2МФБ	0.12	0.5	1.7	0.05	0.08	0.02	60	47	25	8	—60

[1] Treated with synthetic slags and deoxidized with silico-calcium (with reduced sulphur content or sulphur inclusions of globular form).

The weldability of low-alloy pipe steels (in situ welding) is determined practically by what is called the carbon equivalent:

$$C_{eq} = \% + \frac{\%Mn}{6} + \frac{\%(V+Mo+Cr)}{5}$$

which should not exceed 0.46-0.48 (the steels given in Table 16.10 have the following values of C_{eq}: Ст3 — 0.3; 17ГС — 0.48; 14Г2САФ — 0.48; 14Г2СФБ — 0.48; 07Г2ФБ — 0.40; 08Г2МФБ — 0.03). The strength of these low-alloy steels cannot therefore be very high (the guaranteed value is σ_t = 50-60 kgf mm^2). Strength values of 60-70 kgf mm^2 are usually obtained by grain refinement (alloying with niobium nitrides which inhibit grain growth), precipitation hardening (precipitation of disperse vanadium nitrides) and work hardening (ending the rolling operation at a relatively low temperature of 750°C); the last method has been called 'controlled rolling'.

In all these steels, the structure is ferrite + pearlite, with hot-rolled steel having a coarser grain than normalized steel (Fig. 16.18*b* and *c*); after controlled rolling the structure has a marked banded orientation (Fig. 16.18*d*).

Treatment of molten steel with synthetic slags and silico-calcium causes sulphide inclusions to precipitate into a globular form, which increases the impact toughness but raises somewhat the ductile-to-brittle transition point (the sulphide effect, see Ch. 7, Sec. 2).

Strengthening heat treatment (hardening + high-temperature tempering) can produce a higher strength than the methods mentioned above, but this high strength cannot be retained in the heat-affected zone. For that reason, the method turns out to be ineffective with sheets and other steel products of the strength more than 60-70 kgf mm^2. Additional alloying with molybdenum makes a steel suitable for welded structures with the strength σ_t = = 70-80 kgf/mm^2. An example is the popular Fortiweld steel (0.2% C, 0.5% Mo, and 0.003% B).

16.8. REINFORCING STEEL

Reinforcing steels are used for making wire, smooth and Isteg bars and other steel elements for reinforced-concrete and prestressed-concrete structures.

Reinforcing steels of common quality (Ст3, Ст5) are employed in common reinforced concrete structures where the stresses in the metal are not high.

In prestressed-concrete structures, steel elements (bars or wire) are subjected to appreciable stresses and are therefore made of medium- or high-carbon steels by hot rolling with subsequent heat treatment.

Reinforcing steels are divided into several strength classes. Their classification is given in Table 16.11, and the compositions of the most popular reinforcing steels, in Table 16.12.

Classes A-I, A-II and A-III are employed in common reinforced concrete structures and higher classes, in prestressed-concrete structures.

The characteristics corresponding to class A-IV can be obtained in as hot-rolled alloy steels Grades 20ХГ2Ц and 80С and in plain carbon steel Grade Ст5 after strengthening heat treatment (water quenching, tempering at 400°C).

Steel Grade 23Х2Г2Т upon hot rolling and low-temperature tempering (300°C) acquires the properties typical of class A-V. Tempering is mainly done to remove hydrogen from the metal. Steel reinforcement of higher classes (A-VI to A-VIII) is always heat treated to improve the properties.

Table 16.11. Classification of Reinforcing Steels (GOST 5058—65, GOST 10884—71)

Steel class	Properties (minimum values)			Steel Grade	
	σ_t, kgf/mm²	$\sigma_{y\,(0.2)}$, kgf/mm²	δ, %	as hot-rolled	as heat-strengthened
A-I	38	24	25	Ст3	—
A-II	50	30	19	Ст5; 18Г2С	—
A-III	60	40	14	35ГС; 25ГС2	—
A-IV	90	60	6	20ХГ2Ц; 80С	Ст5
A-V	105	80	6	23Х2Г2Т	Ст5; 35ГС
A-VI	120	100	5	—	Ст6; 35ГС
A-VII	140	120	5	—	45С
A-VIII	160	140	4	—	45ГС

Table 16.12. Compositions of Reinforcing Steels, % (GOST 5781—75)

Steel Grade	C	Mn	Si
25Г2С	0.20-0.29	1.2-1.6	0.6-0.9
35ГС	0.30-0.37	0.8-1.2	0.6-0.9
20ХГ2Ц*	0.19-0.26	1.5-1.9	0.4-0.7
80С	0.74-0.82	0.5-0.8	0.6-1.0
45С	0.40-0.48	0.5-0.8	1.0-1.3

* Also contains 0.9-1.2% Cr and 0.07-0.14% Zr.

A steel low in carbon (less than 0.26%) is readily welded by pressure contact welding (which permits a higher carbon content than arc welding). Steels with 0.3-0.4% C are poorly weldable and those with a higher content of carbon are altogether unweldable, mainly because of the loss of ductility in the heat-affected zone. This is why class A-IV contains two steel grades: one weldable and the other, non-weldable.

Steels low in carbon or those upon heat treatment should be preferred for operation at low temperatures.

Steel wires (6-8 mm in diameter) and steel ropes (of wires 1-2 mm in diameter) for prestressed-concrete structures are made of steels with 0.6-0.8% C which acquire a high strength (σ_t up to 180 kgf/mm²) upon strain hardening and heat treatment.

16.9. SPRING STEEL

The operation of springs and similar elements may be characterized by the fact that only the elastic properties of the metal are utilized. The total elastic deformation of a spring may be very large depending

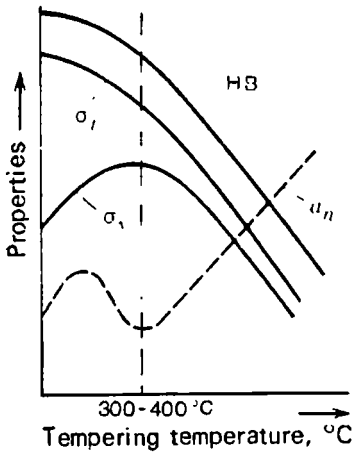

Fig. 16.19. Effect of tempering temperature on mechanical properties

on its design, i.e. the number and diameter of coils, spring length, etc. Since plastic deformation is not allowed in springs, their material should not have a high impact toughness and a high ductility. The main requirement is that the steel has a high elastic limit (yield strength). This is ensured by hardening followed with tempering at temperatures within 300-400°C (Fig. 16.19). Tempering at these temperatures gives the highest value of elastic limit.The fact that this temperature range overlaps the interval of appearance of the first-order temper brittleness is of no great importance for the reasons mentioned earlier.

Springs and like elements are made of structural steels of elevated carbon content (which however is lower than in tool steels), roughly 0.5-0.7% C and often with additions of manganese and silicon. Springs for especially critical applications are made of steel Grade 50ХФ which is alloyed with chromium and vanadium and has the highest elastic properties.

The compositions of selected spring steels are given in Table 16.13.

Heat treatment of alloy-steel springs consists in hardening from 800-850°C (depending on steel grade) with oil or water quenching and tempering at 400-500°C to obtain a hardness of 35-45 *HRC*. This gives a strength of σ_t = 130-160 kgf/mm².

The conditions of heat treatment as recommended by the State Standard GOST 1071—67 for some selected steels of Table 16.13 are given in Table 16.14.

This type of heat treatment is often employed with structural elements of large length or with thin walls of which high elastic properties are required. In such cases, steel Grade 30ХГС is used: upon hardening and tempering at 250°C, it has a strength (σ_t) of 160 kgf mm², but low values of toughness and ductility (a_n = 5 kgf m/cm², δ = 7 per cent, and ψ = 40%).

Springs are often made from cold-drawn polished wire (so-called *silver-steel wire*). Cold drawing produces a work-hardening effect, and therefore, a high strength and elasticity. Upon winding (or other final operation of spring making) springs should be tempered at 250-350°C to remove internal stresses, which will increase the elastic limit. Silver steel wire is usually made of plain carbon tool steels У7, У8, У9, У10.

The state of the surface may have an appreciable effect on the quality and performance of a spring. Cracks, films and other surface defects may become places of stress concentration and of development of fatigue phenomena.

The durability of springs and other elements subjected to alternate stresses can be improved appreciably by surface work-hardening (for instance, by *shot blasting*). This method forms compressive stresses in the metal surface, which raise the endurance (fatigue) limit of a component and diminish the harmful effect of various surface defects.

Table 16.13. Compositions of Spring Steels, %
(GOST 14959—69)

Nos.	Steel Grade	C	Mn	Si	Cr	V
1	65	0.62-0.70	0.50-0.80	0.17-0.37	—	—
2	70	0.67-0.75	0.50-0.80	0.17-0.37	—	—
3	75	0.72-0.80	0.50-0.80	0.17-0.37	—	—
4	65Г	0.62-0.70	0.90-1.20	0.17-0.37	—	—
5	50С2	0.47-0.55	0.60-0.90	1.50-2.00	—	—
6	55С2	0.52-0.60	0.60-0.90	1.50-2.00	—	—
7	60С2	0.57-0.65	0.60-0.90	1.50-2.00	—	—
8	70С3А	0.66-0.74	0.60-0.90	2.40-2.80	—	—
9	55СГ	0.50-0.60	0.80-1.00	1.30-1.80	—	—
10	60СГ	0.55-0.65	0.80-1.00	1.30-1.80	—	—
11	50ХФА	0.46-0.54	0.50-0.80	0.17-0.37	0.80-1.10	0.10-0.20
12	50ХГФА	0.48-0.55	0.80-1.00	0.17-0.37	0.95-1.20	0.15-0.25
13	60С2ХА	0.56-0.64	0.40-0.70	1.40-1.80	0.70-1.00	—

Note. Harmful and occasional impurities not given in the table should not exceed the following values: 0.03-0.04% S; 0.03-0.04% P; 0.3-0.4% Ni; and 0.3% Cr.

Table 16.14. Heat Treatment Conditions for Springs

Steel Grade	Hardening		Tempering, °C	Brinell hardness
	t, °C	quencher		
50С2	870	oil or water	460	365-410
60С2	870	oil	460	390-480
50ХФА	850	oil	520	390-480
60С2ХА	870	oil	420	420-475

Apart from common-purpose spring steels, there are special spring steels for operation under specific conditions (elevated temperatures, aggressive media, etc.). A detailed treatise on spring materials has been written by A.G. Rachstadt.

16.10. BALL-BEARING STEELS

Ball-bearing steels should in the first place have a high hardness, because of which they are usually of the high-carbon tool type (or sometimes low-carbon cemented type). Ball-bearing steels are most often alloyed with chromium to improve their hardening capacity (i.e. to lower the critical rate of hardening) and make the steel suitable for oil quenching.

Selected ball-bearing steels as specified by the State Standard GOST 801—60 are given in Table 16.15.

Table 16.15. Compositions of Ball-bearing Steels, % (GOST 801—60)

Steel Grade	C	Cr	Mn	Si
ШХ6	1.05-1.15	0.4-0.7	0.20-0.40	0.17-0.37
ШХ9	1.05-1.10	0.9-1.2	0.20-0.40	0.17-0.37
ШХ15	0.95-1.05	1.3-1.65	0.20-0.40	0.17-0.37
ШХ15СГ	0.95-1.05	1.3-1.65	0.90-1.20	0.40-0.65

Note. In all these steels, S < 0.020%, P < 0.027%, Ni < 0.3%, and Cu < 0.25%.

In the designation of a steel, the first letter, 'Ш', stands for 'ball-bearing' and the second, X, gives the content of chromium in tenths of a per cent. Chromium is added to ensure the required hardenability. Therefore, smaller elements of bearings can be made of steels with a lower content in chromium.

As has been recommended, balls and rollers of the diameter respectively up to 13.5 mm and 10 mm should be made of steel Grade ШХ9, balls 13.5-22.5 mm and rollers 10-15 mm in diameter, of steel Grade ШХ12, and balls 22.5 mm and rollers 15-30 mm, of steel Grade ШХ15. The last grade is also used to make bearing races, except for very large ones; rollers of the diameter more than 30 mm and races of the wall thickness more than 15 mm should be made of steel Grade ШХ15СГ, which is additionally alloyed with silicon and manganese to increase the hardenability.

In their nature, these chromium steels are similar to carbon steels with roughly 1% C. Chromium is soluble in both phases of annealed steel, i.e. both in ferrite and cementite. Chromium-alloyed cementite dissolves more slowly in austenite and chromium-containing austenite breaks down less quickly, which explains why these steels have a lower critical quenching rate as compared to carbon steels (Table 16.16).

Ball-bearing steels should meet very strict requirements as regards their purity from no-metallic inclusions and carbide segregation. The point is that the stresses acting in ball bearings are local, so that if a ball comes against an inclusion in the bearing race, the metal may be destructed (crumbled out) locally and cause premature failure of the bearing. For that reason, the State Standard GOST 801—60 requires that each melt for ball-bearing steel be carefully checked for porosity, non-metallic inclusions, carbide segregation, and lineage and network structure. The suitability of a steel is checked by referring to a scale of these defects.

Table 16.16. Critical Cooling Rate of Ball-bearing Steels and Critical Diameter of Balls (Rollers)

Steel Grade	Critical quenching rate, °C/s	Critical diameter for oil quenching (95% martensite), mm	Steel Grade	Critical quenching rate, °C/s	Critical diameter for oil quenching (95% martensite), mm
ШХ6	450-500	9-10	ШХ15	35-40	23-25
ШХ9	175-200	14-15	ШХ15СГ	—	50-65

Heat treatment of bearings (balls, rollers and races) includes two operations: hardening and tempering. Hardening is carried out from 830-840°C with oil quenching, which is followed with tempering at 150-160°C for 1 or 2 hours to obtain a hardness value not less than 62 *HRC*. The final structure should be very fine acicular temper martensite with evenly distributed excess carbides (Fig. 16.20). Non-observance of the temperature conditions of heat treatment can impair the quality of bearings and lower their durability.

For instance, even a slight superheating in hardening can coarsen the structure and increase martensitic needles. The steel then becomes brittle and utterly unsuitable for the purpose. Tempering at a temperature higher than 150-160°C results in a lower hardness and thus lowers the wear resistance of bearings. In steel Grade ШХ15, which is the most popular among ball-bearing steels, an increased quantity of retained austenite is often fixed upon hardening (roughly 10-15%), which may transform into martensite in the course of operation and result in unwanted volume changes. To avoid this, precision bearings are subjected to sub-zero treatment with cooling to (—10)-(—20)°C depending on the position of point M_f. Further, bearings for special applications are made of better-quality grades of ball-bearing steel.

Very large roller bearings, 0.5 to 2 m in diameter, are made (both rollers and races) of steel Grade 20Х2Н4А (see its composition in Table 16.2). The rollers and cases made of this steel are cemented to an appreciable depth (5-6 mm, the time of cementation 120-160 hours) and then subjected to a complicated heat treatment which forms the final structure of martensite + carbides in the surface and that of low-carbon martensite in the core.

Bearings for operation in chemically aggressive media are most often made of steel Grade Х18 (0.9-1.0% C, 17-19% Cr, also containing reasonable quantities of manganese, silicon, sulphur, phosphorus, ect.). The high content in chromium is needed to make the steel highly corrosion-resistant. The steel resists

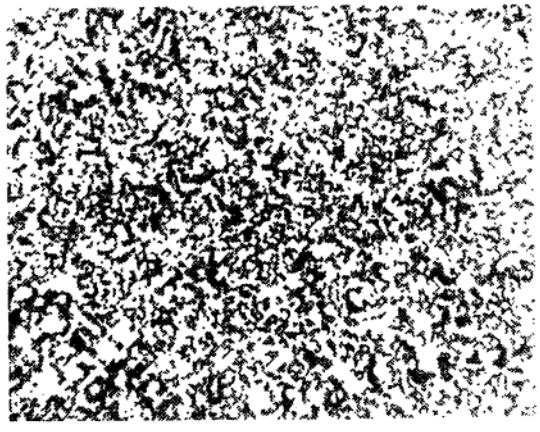

Fig. 16.20. The structure of steel ШХ15 as hardened and tempered, ×500

well the corrosion in sweet and sea water, solutions of nitric and acetic acids and various organic media, but its corrosion resistance is poor in mixtures of nitric and sulphuric acids.

The heat treatment to the maximum hardness and an appropriate dimensional stability includes oil quenching from 1 050°C, freezing at —70°C, and tempering at 150-160°C to a hardness of 60-61 *HRC*.

Bearings to operate at elevated temperatures (up to 400-500°C) are made of steels of the high-speed type (to be discussed later in the book). Usually steel Grade P9 is employed for the purpose, but with somewhat lower contents in carbon and vanadium. A lower carbon content is essential to diminish carbide segregation, which might impair the durability of bearings. Bearings made of this steel are heat treated in the same manner as high-speed steel tools (to be discussed later).

16.11. DEFECTS IN ALLOY STEELS

Because of their high mechanical properties, alloy steels find preferable application over carbon steels in many branches of special machine-building (aircraft engineering, motor vehicle construction, etc.). On the other hand, alloy steels are more often than carbon steels infected with various defects. In many cases, these defects cannot be removed even under strict observance of the process specifications. The most important types of defects in steel are *temper brittleness*, *dendritic segregation*, and *flakes* (the phenomenon of temper embrittlement has been discussed in Sec. 16.2).

Dendritic segregation. The appearance of dendritic segregation is due to non-uniform crystallization in a melt (see Sec. 5.10). The alloying elements which are present in a steel widen the temperature interval of crystallization, impede the diffusion processes, and increase the difference of concentrations between earlier and later precipitated crystals and thus promote dendritic segregation (according to I.N. Golikov). The macrostructure of a steel with dendritic segregation is shown in Fig. 16.21*a*.

Upon rolling or forging, dendritic segregates are stretched into fibres oriented in the direction of the deformation (Fig. 16.21*b*). The presence of deformed non-metallic inclusions (see Fig. 16.17) results in some mechanical properties of the metal ($\sigma_{0.2}$, ψ, a_n) being lower across fibres than along them. The phenomenon is called the *anisotropy of mechanical properties*[1].

In order to minimize dendritic segregation, ingots before rolling are often subjected to diffusion annealing which consists in a long heating at a rather high temperature (1 000-1 200°C).

Flakes. Flakes are seen as spots in a fracture (Fig. 16.22) and as cracks, in a cross-cut microsection. Naturally, the presence of cracks worsens the mechanical properties. Flakes are more dangerous in

[1] Anisotropy can be diminished by refinement of the steel from non-metallic inclusions, especially of the sulphide type, by metallurgical techniques (treatment with synthetic slags, electroslag remelting, etc.).

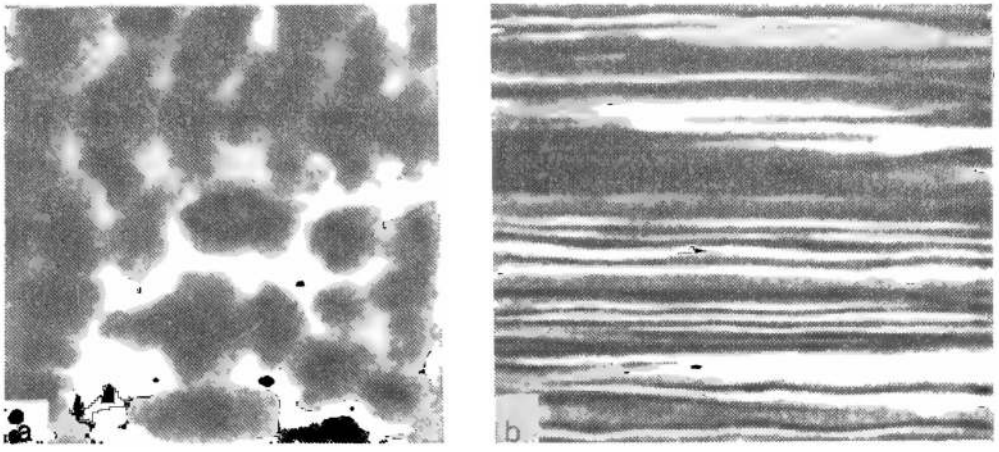

Fig. 16.21. Defects of macro- and micro-structure in alloy steel. × 130 (A. Sauveur)

(*a*) dendritic segregation; (*b*) lineage structure

steels of higher ultimate strength and are a very serious defect in high-quality steels. Flakes may form in all steels, but most often they appear in chromium-containing steels, i.e. Cr, Cr-Ni, Cr-Ni-W, Cr-Mn grades and the like.

Flakes are often found in forged and rolled steel and only rarely, in cast steel.

When can flakes appear in steel?

Flakes can form in a flake-sensitive steel if this has been cooled quickly near 200°C upon forging or rolling. At temperatures above 200°C, cooling rate has no effect on flake formation. Thus, flakes can form during quick cooling from 200° to 20°C.

There is some evidence that flake formation may be attributed to the presence of hydrogen in molten steel, which precipitates from the solution at temperatures below 200°C and causes strong internal stresses which result in internal cracks (flakes). If a steel is cooled slowly, hydrogen has enough time for diffu-

Fig. 16.22. Flakes in steel (fracture)

sion from the solution and escapes from the steel. The resulting steel is free from flakes (S. S. Steinberg, E. Houdremont).

Thus, the main cause of flakes is the hydrogen which is dissolved in steel and has no time to escape at temperatures below 200°C.

Flakes are formed only rarely in cast steel, since the hydrogen that liberates from the solution is accumulated in numerous casting pores and loose portions of the cast metal.

Flakes can be eliminated by forging or rolling to a smaller size in which they are welded in. Flakes are seldom found in parts of small cross-section (less than 25-30 mm in diameter).

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Chapter 17

TOOL STEELS

17.1. GENERAL

The principal requirement imposed upon steels for cutting tools is that the cutting edge remained sharp for a long time. During operation, the cutting edge is worn off and becomes blunt. In contrast to wear-subjected machine elements (shafts, cams, etc.), a cutting tool is subjected to wear only on a very narrow band of metal, with the pressure exerted on that band being quite appreciable. The band should therefore have a high hardness (usually above 60 *HRC*) to be wear resistant.

In the cutting of soft materials (wood, plastics, non-ferrous metals), and also in the machining of steel and cast iron at low cutting speeds, the chip is rather thin and the energy spent in the cutting process is low. On the other hand, machining at high speeds or of hard materials with thick chip requires a high energy. During the cutting process, the mechanical energy is converted to heat and the cutting edge may be heated appreciably (red-hot) under severe cutting conditions. The principal requirement of such a tool is to retain its hardness during long heating, i.e. its steel should possess an adequate red hardness.

The service conditions of measuring instruments are similar, to a definite extent, to the operating conditions of cutting tools under light cutting conditions, though the pressures on the working surfaces are appreciably lower.

The steel in dies is subjected to substantial thermal and impact loads which are distributed over a relatively large area. Here, the toughness of the die metal becomes essential. The best steel for dies is that having the optimum combination of hardness and toughness at the temperature conditions of die operation.

Thus, various types of tool require steels with different properties. All tool steels are classed into four categories: (1) steels of reduced hardenability (mostly carbon steels); (2) steels of elevated hardenability (alloy steels); (3) die steels; and (4) high-speed steels.

A special group of tool materials is formed by hard alloys which are employed in tools operating at especially high cutting speeds.

Carbon and alloy steels are used for making cutting tools for light operating conditions and for making measuring instruments. High-speed steels find application in cutting tools operating under more severe cutting conditions.

17.2. TOOL STEELS OF REDUCED HARDENABILITY

This group includes all carbon tool steels and also some alloy steels having a low content of alloying elements and therefore essentially the same hardenability as the former. All these steels are combined into a single group by a very important property, i.e. the ability to be hardened only to a shallow depth.

All steels of the group should be quenched in water. Tools made of them usually have an unhardened core. These circumstances should be taken into account when selecting a particular grade of steel or in the design, heat treatment and application of the tools[1].

The compositions of tool steels of reduced hardenability are given in Table 17.1.

Table 17.1. Composition of Tool Steels of Reduced Hardenability (GOST 1435—74, GOST 5950—73)

Steel Grade	C	Mn	Cr	Steel Grade	C	Mn	Cr
У7	0.65-0.74	0.20-0.40	< 0.15	У13	1.25-1.35	0.15-0.35	< 0.15
У8	0.75-0.84	0.15-0.40	< 0.15	Х05	1.25-1.40	0.20-0.40	0.4-0.60
У9	0.85-0.94	0.15-0.35	< 0.15	Х06	1.05-1.14	0.40-0.70	0.4-0.60
У10	0.95-1.04	0.15-0.35	< 0.15	65ХФ	0.60-0.70	0.30-0.60	0.45-0.70
У11	1.05-1.14	0.15-0.35	< 0.15	85ХФ	0.80-0.90	0.30-0.60	0.45-0.70
У12	1.15-1.24	0.15-0.35	< 0.15				

Notes: 1. In all these steels the contents of impurities should not exceed: silicon 0.30-0.35%; nickel 0.2%; sulphur and phosphorus 0.02% in high-quality steels (group A) or 0.03% in quality grades.
2. Steel Grades 65ХФ and 85ХФ contain 0.15-0.30% V.

As may be seen, carbon tool steels are graded У7, У8, У9, etc., where the letter 'У' stands for carbon and the digit after it gives the average specified carbon content in tenths of a per cent (that is, steel Grade У7 contains 0.7% C, Grade У8, 0.8% C, etc.).

The right-hand portion of the table gives compositions of alloy tool steels, which differ from the carbon tool steels in a higher content of manganese and in that they are alloyed with roughly 0.5% Cr.

[1] For instance, water quenching requires special measures to prevent warping of tools; when designing the tools, sharp corners and abrupt changes in cross-section should be avoided.

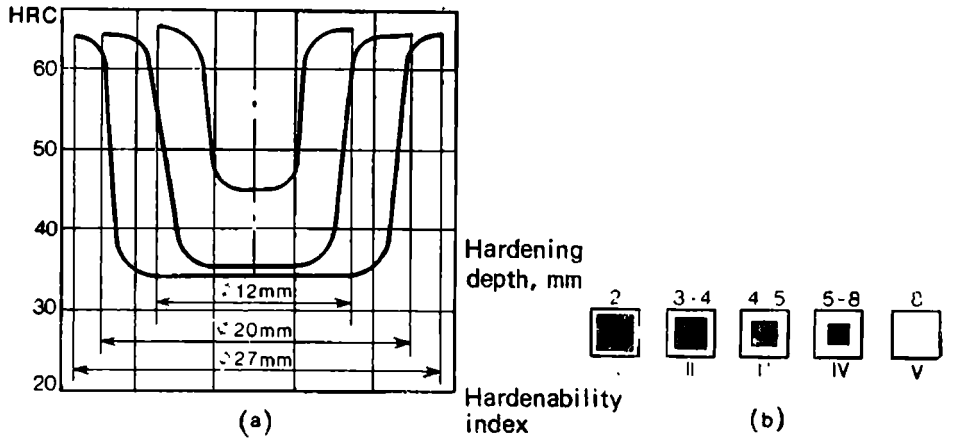

Fig. 17.1. Hardenability of carbon tool steel

(*a*) steel Grade У12 water quenched from 790°C; (*b*) hardenability scales

As has been emphasized, a shallow hardening depth is the most typical feature in these steels. Figure 17.1*a* shows curves of hardness distribution over the cross-section of bars 12, 20 and 27 mm in diameter. As may be clear from the curves, steel Grade У12 cannot be hardened to martensitic hardness in the core even by intensive water quenching, i.e. it cannot be hardened through even in thin sections 12 mm in diameter.

Experience shows that the hardenability of these steels is rather unstable. Individual melts of the same steel grade may differ appreciably from each other in their hardenability. In some melts, square rods (20 × 20 mm) may be hardenable to the entire depth, whereas rods from another melt will be hardenable only to a depth of 1 or 2 mm. This is why carbon and alloy tool steels of reduced hardenability are checked for hardenability by using a 5-index scale (Fig. 17.1*b*). Specimens 20 × 20 mm in cross-section are quenched in water from 800°C and the depth of hardened zone is examined in the fracture.

Steels having the hardenability of index I or V should be avoided; the former are susceptible to soft spotting on the surface and the latter, to cracking.

Experimental studies and practice of tool hardening have shown that the best results are obtained when the hardness of unhardened core is 40-45 *HRC*. At a higher hardness, cracks are likely to appear on the surface; at a lower hardness, internal annular cracks in the transient zone are probable. Since the hardness in the core depends on the size of tool (Fig. 17.1*a*), as well as on the hardenability of the tool steel and the conditions of quenching, these factors should be balanced so as to obtain a hardness of 40-45 *HRC* in the core.

The properties of carbon tool steels and the conditions of their heat treatment are mainly determined by the content in carbon.

Steel Grade У7А is hypoeutectoid steel and is hardened from a temperature above point Ac_3. Steel Grades У8А and У9А are eutectoid steels. The structure of steels У7, У8 and У9 in as-hardened state consists solely of martensite.

The hardening temperature for hypereutectoid steels У10А and У12А lies in the range between Ac_3 and Ac_1; their structure as hardened is martensite + excess (secondary) carbides (see Fig. 11.2*b*). The optimum temperatures of hardening for these steel grades are given in Fig. 17.2.

In as-hardened steel, the tetragonality of the martensite and the internal stresses produce an appreciable brittleness, so that tempering after hardening is indispensable. The tempering temperature is determined by the working hardness desired in the tool. The recommended tempering temperatures for some types of tool are given in Table 17.2.

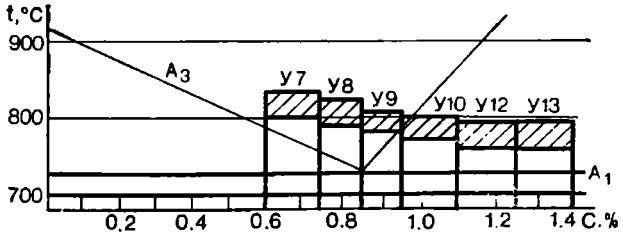

Fig. 17.2. Hardening temperatures for carbon tool steels

Among the steels mentioned in Table 17.2, Grade У7А is the softest and most ductile and is employed in tools subjected to impacts during operation. The hardness of the other steels in as-hardened state is independent of carbon

Table 17.2. Tempering Temperature for Various Tools Made of Carbon Steel

Type of tool	Steel Grade	Tempering temperature, °C	Hardness of working portion, *HRC*
Screw taps	У10-У12	180-200	60-62
Reamers	У10-У12	160-180	62-64
Chisels	У7	280-300	56-58
Cold-stamping dies	У8-У10	200-220	60-62
Screw dies	У10	220-240	59-61

content, but their wear resistance increases at a higher content of carbon, which may be explained by the inclusions of excess cementite in the martensite.

The steels described may have approximately the following applications.

Grade У7: in tools subjected to impacts and shocks in which an appropriate toughness is needed at a moderate hardness (chisels, forging dies and tools, brand stamps).

Grade У8: in tools subjected to impacts and requiring a good toughness and a high hardness (upper and lower dies, metal-cutting shears and cutters, carpenter's tools, pneumatic tools).

Grades У9 and У10: in tools not suffering from large shocks but requiring the highest hardness in the cutting edge, such as various metal-cutting tools (drills, screw taps, reamers, cutters, mill cutters, etc.), coinage dies, drilling tools, medical tools, knives for cutting paper, leather, etc.

Grades У12 and У13: in tools where the maximum wear resistance and maximum hardness are needed, such as cutters, various metal-cutting tools and measuring instruments, files, file-cutting chisels, engraving tools, drawing plates, etc.

Grades 85ХФ, Х06 and Х05: for the same purposes as Grades У9, У11 and У13. A slight percentage of chromium (around 0.5%) in these steels prevents graphitization and soft spotting on the surface (owing to a deeper hardenability). Chromium-alloyed steels have a finer grain since the chromium-containing cementite is more stable against dissolution and the presence of undissolved carbides in it inhibits the growth of austenitic grains. Steel Grade 85ХФ, which also contains vanadium, is quite fine-granular and tough and is employed mainly in wood-cutting tools.

Tool steels are delivered as semi-products (bars, strip, wire, forgings, etc.) and should be annealed to granular pearlite to have a good machinability (a steel having a structure of lamellar pearlite is poorly machinable). Annealing should be done so as to form cementite grains of moderate size (3-4 μm) and evenly distributed in the steel. This structure can be obtained most easily by annealing at a temperature slightly above Ac_1.

17.3. TOOL STEELS OF ELEVATED HARDENABILITY (ALLOY TOOL STEELS)

This group combines tool steels containing 1 to 3 per cent of alloying elements and having an elevated hardenability. Tools made of these steels can be quenched in oil (or in salt baths in stepwise hardening) and are usually through hardened.

The moderate quenching rate in hardening diminishes the risk of cracking, deformation and warping in these steels as compared to carbon tool steels. This aspect is of great importance for many tools of intricate shape.

Alloying with various elements makes it possible to control the hardness, wear resistance and resistance to tempering. In that connection alloy tool steels are classed into three groups, as may be seen from Table 17.3.

Table 17.3. Composition of Tool Steels of Elevated Hardenability, % (GOST 5950—73)

Steel Grade	C	Mn	Si	Cr	W	V
			Group I			
X	0.95-1.1	< 0.4	< 0.35	1.3-1.6	—	—
9XC	0.85-0.95	0.3-0.6	1.2-1.6	0.95-1.25	—	—
ХГСВФ	0.95-1.02	0.7-1.0	0.7-1.0	0.6-1.0	0.8-1.1	0.08-0 15
			Group II			
ХГ	1.3-1.5	0.45-0.7	< 0.35	1.3-1.6	—	—
ХВГ	0.9-1.0	0.8-1.0	0.15-0.35	0.9-1.2	1.2-1.6	—
			Group III			
В1	1.05-1.25	0.2-0.4	< 0.35	0.10-0.30	0.8-1.2	—
ХВ5	1.25-1.50	< 0.3	< 0.30	0.40-0.70	4.5-5.5	0.15-0.30

Group I includes common alloy tool steels in which the hardenability is increased by alloying with 1.0-1.5% Cr. An addition of silicon gives a further increase in hardenability and also increases the temper resistance (thermal stability) and thus improves the serviceability of tools.

Let this be illustrated by the data as follows.

Table 17.4 gives critical diameters for water and oil quenching[1] of steels У10, X, and 9XC. The values in the table are the maximum diameters of rods (parts) at which the hardness in the core on quenching from common hardening

[1] These data can be used when selecting the quencher and the maximum diameter for some tools of elevated hardenability.

Table 17.4. Hardenability of Tool Steels

Steel Grade	Critical diameter for quenching, mm	
	in water	in oil
У10	6-10	2-3
X	30-40	15-20
9XC	40-50	20-25

temperatures in water or oil is almost equal to that in the surface, i.e. not less than 60 *HRC*.

To obtain a desired hardness in a steel alloyed with chromium and especially in one alloyed with chromium and silicon, it should be tempered at a higher temperature than that recommended for carbon steels (Fig. 17.3). This also means that heating of the cutting edge in operation is less dangerous for steel 9XC than for Grade X or У10. Steel Grade X has exactly the same content of carbon and alloying elements as ball-bearing steel ШХ15, but may be more contaminated with non-metallic inclusions and have more other defects of metallurgical origin. Therefore, steel Grade ШХ15 can substitute Grade X in all cases (but not the other way).

An elevated content of silicon in steels of this type (up to 1.6% in steel 9XC) involves certain difficulties in the manufacture. Steel 9XC is more liable to decarbonization on hardening, since silicon raises the critical points; this is why silicon-containing steels should be heated for hardening to a higher temperature at which the processes of surface decarbonization can occur more quickly.

Group II of alloy tool steels can be characterized by an elevated content in manganese (at a moderate content of silicon). This increases the percentage of retained austenite on hardening and lowers deformation; for that reason these steels can be called low-deformable tool steels.

Group III includes high-hardness steels which are usually alloyed with tungsten. They have a poorer hardenability than groups I and II and for that reason could be related to the category of steels of reduced hardenability which has been discussed in the previous section.

Alloying with tungsten refines appreciably the excess carbide phase and therefore increases the hardness of these steels. They can be quenched in water or oil (in the latter case, parts up to a definite critical section). Water quenching gives a higher hardness. For instance, steel Grade B1 upon water quenching (and tempering at 100-120°C) may have a hardness of 67-68 *HRC* and steel XB5, up to 69-70 *HRC*, whereas oil quenching (and the same tempering) gives a hardness not above 64-65 *HRC*. This difference can be explained by the fact that less retained austenite is formed in the former case and that the initially formed martensite has no time (with fast quenching) for tempering in the martensitic transformation range[1].

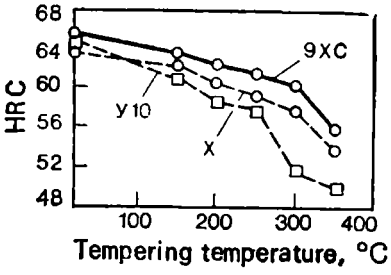

Fig. 17.3. Effect of tempering temperature on hardness of steels У10, X, and 9XC

[1] The M_s point of these steels lies near 250°C, because of which first portions of the martensite which form at the beginning of the martensitic range can decompose if the cooling rate is low (as in oil quenching).

Table 17.5. Heat Treatment Conditions for Alloy Tool Steels

Steel Grade	Annealing		Hardening			Tempering	
	temperature, °C	*HB*	temperature, °C	quencher	*HRC* (minimum value)	temperature, °C	*HRC*
X	770-790	225-207	830-860	Oil	62	150-200	64-61
9XC	790-810	255-207	820-860	Ditto	62	140-160	65-62
						160-180	63-61
ХГСВФ	790-810	228-196	820-850	Ditto	—	140-160	63-61
			840-860	Ditto	62	160-180	61-59
ХГ	780-800	241-197	800-830	Ditto	61	150-200	64-61
ХВГ	770-790	255-207	800-830	Ditto	62	140-160	65-62
						170-200	62-60
В1	780-800	229-187	800-850	Water	62	150-200	64-62
ХВ5	730-750	321-255	800-820	Ditto	65	100-120	66-64
						120-160	65-61

Note. The hardness after hardening is given as guaranteed by GOST; the hardness after tempering is given within the common range of variation.

The high hardness of these steels is utilized for machining very hard materials (such as stone) or when it is desired to have a sharp cutting edge for a long time (in cutting at low speeds).

The recommended conditions of heat treatment for the steels indicated in Table 17.3 are given in Table 17.5; the table also gives the hardness values obtained.

The hardening temperatures for these steels are somewhat higher than for carbon tool steels, which is mainly due to the alloying with chromium, tungsten and silicon; these elements raise the critical points and retard the dissolution of carbides. The carbide phase in these steels is M_3C carbide (cementite alloyed with chromium, tungsten and manganese). In steel XB5, M_3C carbide is the dissolved carbide phase and M_6C, the excess phase.

Tools made of these steels are tempered so as to obtain the desired hardness and toughness. If the maximum hardness is needed, the temperature of tempering should not exceed 150-160°C (and the hardness value thus obtained will be not less than 62 *HRC*); if a greater toughness is desirable, the tempering temperature is sometimes raised up to 300°C, but this inevitably involves a drop in hardness to 55-60 *HRC* (depending on steel composition, see Fig. 17.3).

Applications of tool steels are summarized in Table 17.6.

17.4. HIGH-SPEED STEELS

High-speed steels are employed in cutting tools operating at high speeds and therefore should in the first place be capable of remaining hard when hot, i.e. should possess an appropriate red hardness.

Table 17.6. Applications of Tool Steels

Type of tool	У8-У12	В1, В2	Х, Х9	9ХС	ХГ	ХВ5	Х12ФМ, Х12Ф1	5ХНС, 5ХНВ	4ХС, 4ХВС	7Х3	3ХВ8, ЭИ160	High-speed steels
Metal-cutting tools (for light cutting)	+		+	+								
Metal-cutting tools (for heavy cutting)												+
Files	+		+									
Metal saws	+	+										+
Gauges	+		+		+		+					
Tools not to be deformed on hardening			+	+	+		+					
Tools for diamond boring						+						
Hammer dies	+							+	+	+	+	
Upsetting and embossing dies	+								+			
Cold-stamping dies	+	+	+	+	+		+					
Die plates	+											
Pressure-casting dies	+								+		+	

Before dealing with the properties and heat treatment of high-speed steels, let us consider the conditions of operation of a tool made of this steel. Take a cutter as the simplest example[1]. In the cutting process, the cutter removes chips from the surface of the material being machined. This requires a definite amount of mechanical work, which is transformed into heat. The heat is spent to heat up the blank, chips and cutter, and part of it is dissipated to the atmosphere.

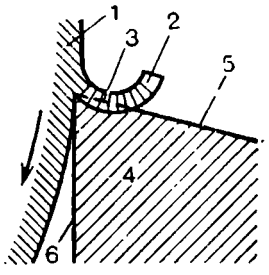

Fig. 17.4. A crater formed in a cutter by abrasion of chip

1 — material being machined; *2* — chip; *3* — crater; *4* — cutter; *5* — front surface; *6* —rear surface

During the machining process, the body of the blank wears off the rear surface of the cutter and the on-running chip wears off the front face (Fig. 17.4). The rear surface is worn off only insignificantly, but the front face is worn substantially and soon a crater forms in it. At some moment, the neck between the front and rear faces of the cutter becomes so thin that the cutter cannot withstand the pressure of the chip and the cutting edge breaks instantaneously.

The durability of a cutter depends on how quickly a crater can form in it, which in turn depends on the wear resistance of the cutter steel in the heated state and the temperature of its heating.

The heating temperature of cutters depends on the conditions of machining. At a higher productivity, the cutter removes more chip per unit time; at a higher resistance to deformation of the material, the cutting edge of the cutter is heated more. In the most heated portion of a cutter, the temperature may reach 600 to 700°C. If this temperature does not soften the tool steel, the cutter will retain its wear resistance and cutting ability for a long time.

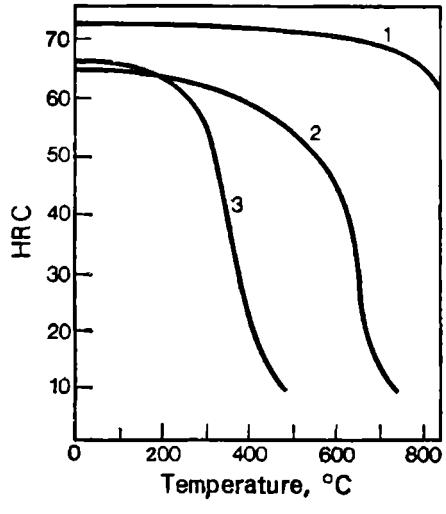

Fig. 17.5. Hardness of various tool materials in heated state

1 — hard alloy; *2* — high-speed steel; *3* — carbon steel

It may be taken to a first approximation that the wear resistance of a cutter is characterized by the hardness of the cutter steel in a heated state. Therefore, steels for cutting tools should be capable of retaining a high hardness at elevated temperatures.

Figure 17.5 shows the temperature-hardness curves for three various alloys. As may be seen, the hardness of the car-

[1] Though our considerations are equally valid for other types of cutting tool.

bon steel drops down quickly upon heating to 200°C. Therefore, this steel cannot be employed under cutting conditions with heating above 200°C. The high-speed steel retains its high hardness on heating to 500-600°C. Thus, a tool made of high-speed steel is more productive than that of carbon steel. A tool made of a hard alloy will be even more productive, since its hardness is not affected at temperatures up to 800°C.

It should be noted that the hardness value in the cold state can by no means determine the cutting ability of a steel. As may be seen from Fig. 17.5, the hardness of the carbon steel at room temperature is even higher than that of the high-speed steel, but its cutting ability is far lower. A high hardness is always essential in tool steels, but high-speed cutting tools should have a high hardness at elevated as well as at room temperature. Further, a good high-speed steel should retain its high hardness for a long time when heated. In other words, a high-speed steel should retain its hardness when heated, i.e. should possess what is called *red hardness.*

Consider certain relationships existing between temperature, hardness and structural changes in high-speed steel (the theory of red hardness).

Heating always causes a reduction in hardness, but the process is reversible as long as no structural changes take place in the steel, i.e. the hardness of the steel will return to the original value on cooling to the initial temperature (see curve *1* in Fig. 17.6).

If however heating causes certain structural changes which lower the hardness (the vertical arrow in Fig. 17.6*a* or the curve in Fig. 17.6*b*), the material will have a lower hardness on cooling to the initial temperature. The resistance to these irreversible structural changes characterizes the red hardness.

What characteristics of the structure do determine the high red hardness of hardned steels?

The high hardness of martensite is due to the dissolution of carbon in α Fe. Tempering of carbon steel is known to cause precipitation of finest carbide particles from martensite. As long as the precipitated carbides remain finely disperse (i.e. at the initial stage of precipitation in tempering at 200°C), no noticeable changes occur in the hardness. If however, the tempering temperature is raised above 200°C, carbide precipitates grow in size and hardness drops down quickly.

Thus, in order to make a steel capable of retaining its hardness on heating, it should be alloyed with elements which can inhibit the process of carbide coagulation.

If a carbide-forming element is added to a steel in an amount sufficient to form a special carbide, the red hardness of the steel will rise jumpwise. The point is that the special carbide can precipitate from martensite and coagulate at a higher temperature than that

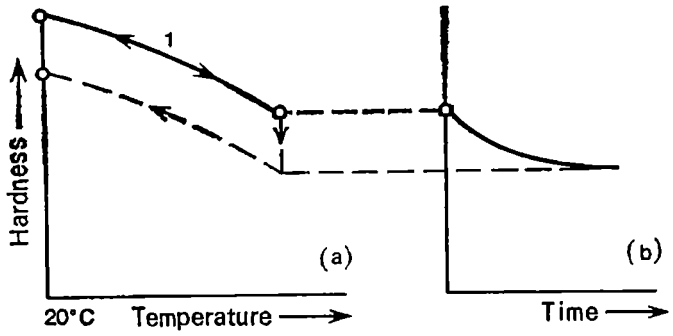

Fig. 17.6. Variations of hardness of high-speed steel in heating (schematic)

needed for iron carbide, since the process is based on the diffusion of alloying elements, as well as on the diffusion of carbon. Practically, special carbides of chromium, tungsten, molybdenum and other elements begin to coagulate noticeably at temperatures above 500°C.

Thus, a *high red hardness can be ensured in a steel by alloying it with carbide-forming elements (tungsten, molybdenum, chromium, vanadium) in an amount sufficient to combine almost the entire carbon into special carbides.*

Among high-speed steels, the most popular Grades are P18 (0.7% C, 18% W, 4% Cr, and 1% V) and P6M5 (0.9% C, 6% W, 5% Mo, 4% Cr, and 2% V).

The compositions of high-speed steels as specified by the State Standard GOST 19265—73 are given in Table 17.7.

All high-speed steels are designated by a letter 'P' and digits giving the content of the main alloying element, tungsten, or of tungsten and molybdenum in W-Mo steels. With a heavy alloying with vanadium or cobalt, their content is designated respectively by letters 'Ф and K and the corresponding digits. All high-speed steels contain roughly 4 per cent chromium and their carbon content is balanced with that of vanadium (more vanadium requires more carbon).

Steel P18 is the most popular general-purpose grade of high-speed steel. Steel Grade P9 has similar cutting properties and applications, but involves greater difficulties in heat treatment, in particular, more rigorous observance of hardening conditions, and in addition has a poor grindability. Steel P18 is more expensive, but possesses high mechanical characteristics. Yu. A. Geller has developed steel Grade P12 (with 12% W) which is free of the above disadvantages. Cobalt-alloyed high-speed steels are highly productive cutting-tool steels which can be employed for cutting poorly machinable materials or when their higher cost is justified by the better cut-

**Table 17.7. Composition of High-speed Steels, %
(GOST 19265—73)**

Steel Grade	C	Cr	W	V	Mo	Co
P18	0.7-0.8	3.8-4.4	17.0-18.5	1.0-1.4	1.0	—
P12	0.8-0.9	3.1-3.6	12.0-13.0	1.5-1.9	0.5	—
P9	0.85-0.95	3.5-4.4	8.5-10.0	2.0-2.6	1.0	—
P6M3	0.85-0.95	3.0-3.6	5.5-6.5	2.0-2.5	3.0-3.6	—
P6M5	0.80-0.88	3.8-4.4	5.5-6.5	1.7-2.1	5.0-5.5	—
P18Ф2	0.85-0.95	3.8-4.4	17.5-19.0	1.8-2.4	1.0	—
P14Ф4	1.2-1.3	4.0-4.6	13.0-14.5	3.4-4.1	1.0	—
P9Ф5	1.4-1.5	3.8-4.4	9.0-10.5	4.3-5.1	1.0	—
P18K5Ф2	0.85-0.95	3.8-4.4	17.5-19.0	1.8-2.4	1.0	5.0-6.0
P10K5Ф5	1.45-1.55	4.0-4.6	10.0-11.5	4.3-5.1	1.0	5.0-6.0
P9K10	0.9-1.0	3.8-4.4	9.0-10.5	2.0-2.6	1.0	9.5-10.5
P9M4K8	1.0-1.1	3.0-3.6	8.5-9.5	2.1-2.5	3.8-4.3	7.5-8.5

Note. The content of permanent and occasional impurities in these steels is limited at 0.4% Mn, 0.5% Si, 0.4% Ni, 0.03% S, and 0.035% P.

ting properties. It should be added that vanadium-rich high-speed steels are superior over P18 mainly due to their higher wear resistance, whereas cobalt-rich steels are superior owing to their higher red hardness. On the other hand, high-vanadium steels have a poor grindability (which often involves difficulties in the manufacture of tools), and cobalt-rich steels have poorer mechanical properties.

In view of the deficiency of tungsten, W-Mo steels have recently found a wide application and even replaced the 'classical' P18 steel. Among them, steel Grade P6M5 is the most popular.

The structure of a high-speed steel, as annealed, consists of carbides and α-solid solution. Three types of carbide: M_6C, MC and $M_{23}C_6$ occur in high-speed steels; their composition is the same in all steel grades (Table 17.8), but the total quantity and proportion may be different (Table 17.9)[1].

[1] According to some researchers, other types of carbide, such as M_2C, $M_{23}C_6$ or M_7C_3, can be present in certain grades of high-speed steel under definite conditions; these results are however disputable, since the content of these carbides, as given by the authors themselves, is not high and their presence does not change substantially the processes occurring in the steel.

Table 17.8. Analysis of Carbides Occurring in High-speed Steels, %

Carbide	C	W	V	Cr	Fe
M_6C	2	65	3	3	27
MC	12	42	43	2	1
$M_{23}C_6$	5	10	3	47	35

Table 17.9. Carbide Phase in High-speed Steels

Steel Grade	Quantity, %	Composition	Steel Grade	Quantity, %	Composition
P18	29	M_6C	P9Ф5	21	M_6C+MC
P12	24	M_6C+MC	P18K5Ф2	29	M_6C+MC
P9	18	M_6C+MC	P10K5Ф5	24	M_6C+MC
P6M3	19	M_6C+MC	P9K5	18	M_6C+MC
P6M5	21	M_6C+MC	P9K10	18	M_6C+MC
P18Ф2	29	M_6C+MC	P6M5K5	21	M_6C+MC
P14Ф4	22	M_6C+MC	P9M4K8	22	M_6C+MC

Note. Upon annealing.

Steel P18 contains M_6C carbide and the other high-speed steels contain M_6C and MC carbides, with MC to M_6C ratio increasing with increasing content in vanadium (for instance, steel P9 has 15% MC carbide and 85% M_6C carbide and steel P9Ф5, as much as 40% MC). Probably all these steels also contain 2-3% $M_{23}C_6$ carbide (not indicated in Table 17.8).

All high-speed steels are similar in their nature and differ only in the rate of transformation processes and the thermal stability; thus, their nature can be analysed by taking, say, steel Grade P18 as an example.

Steel P18 (sometimes designated 18-4-1, the digits referring to the content of tungsten, chromium and vanadium, respectively) contains only one type of carbide, M_6C, so that the transformation processes in it can be analysed by considering the pseudo-binary Fe-M_6C constitutional diagram shown schematically in Fig. 17.7. When the melt is cooled and solidifies, carbides should gradually precipitate from the solution. Primary carbides enter the composition of the eutectic (which is usually called ledeburite). In tungsten high-speed steels, the eutectic is of a 'skeleton-like' shape, i.e. with carbide platelets interlaced with austenite (Fig. 17.8*a*). During cooling after solidification, secondary carbides precipitate from austenite, since their solubility in austenite diminishes with tempera-

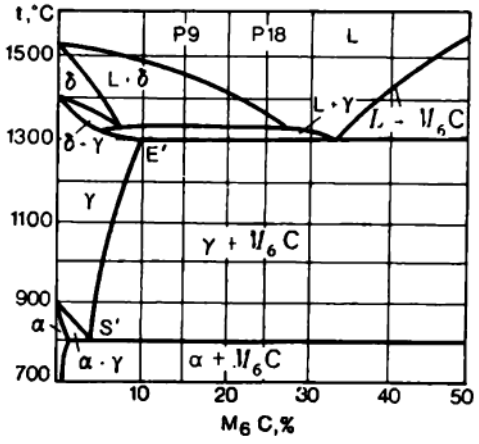

Fig. 17.7. Pseudo-binary Fe-M_6C constitutional diagram (schematic)

ture (line $E'S'$ in Fig. 17.7). Finally, pearlitic transformation begins at the temperature A_1 (800°C), i.e. the austenite breaks down into alloyed ferrite and fine (eutectoid) carbides.

If the cooling process has been insufficiently slow (a common case), the peritectic $L + \delta \rightarrow \gamma$ transformation has no time to proceed to the end and the phase called δ-ferrite is retained in the metal at room temperature. It is seen in the microstructure of cast high-speed steel (Fig. 17.8*a*) as dark rounded-off crystals.

Forging deformation changes the structure of high-speed steel by disintegrating the eutectic into separate carbide particles. Three types of carbide can be observed in forged and annealed steel: large separate primary carbides, finer secondary carbides, and very fine eutectoid carbides which constitute the main sorbitic background (the sorbitic background is formed by the mixture of ferrite and eutectoid carbides), see Fig. 17.8*b*.

Heating of high-speed steel up to the critical point Ac_1 (800°C) involves no structural changes. On passing through the critical point, the eutectoid transforms into austenite. In further heating, secondary carbides are dissolved in the austenite and the latter is saturated with carbon and alloying elements.

The curves in Fig. 17.9 show how the austenite of high-speed steel P18 is saturated with alloying elements as the temperature increases.

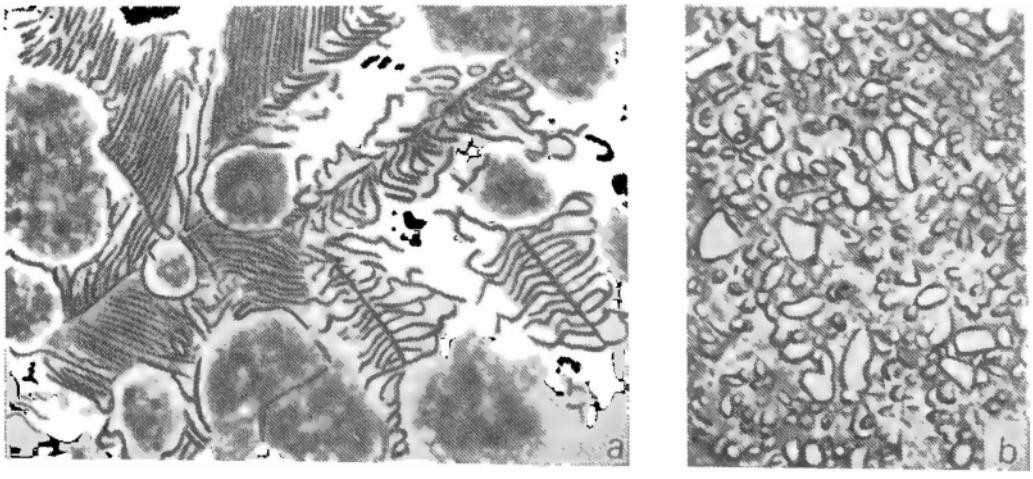

Fig. 17.8. Microstructure of high-speed steel. ×1 000
a) as cast (ledeburitic eutectic); (*b*) as forged and annealed

As may be seen from the diagram, hardening from a relatively low temperature, say 1 100°C, gives only a slight saturation of austenite with tungsten (less than 3%).

In hardening, austenite transforms into martensite with the same content of alloying elements. Therefore, the martensite formed from a high-alloyed austenite will also be high-alloyed and ensure a higher red hardness, and therefore, a higher durability. These data also suggest that high-speed steels should be hardened from as high a temperature as possible if high-alloyed stable martensite is desired (on hardening from 1 200°C the solution will contain 7% W).

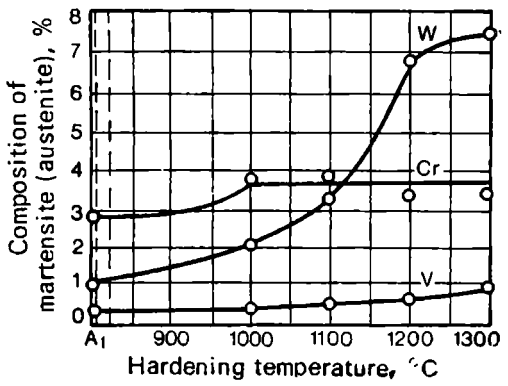

Fig. 17.9. Effect of temperature on the composition of austenite (martensite) in steel P18 (the author)

Note that primary carbides are not dissolved in the austenite even at the highest temperature of hardening. Steel Grade P18 differs from Grade P9 only in that it has a higher content of primary excess carbides; for the same temperature of hardening, the saturation of austenite, and therefore, the composition and red hardness of martensite, will be the same in both grades. For that reason, the two grades have practically the same cutting properties notwithstanding the wide difference in their composition.

If a steel is alloyed with cobalt, the latter can partially substitute iron atoms in M_6C carbide and thus produce a more complex carbide, which inhibits the process of coagulation, and therefore, increases the red hardness and cutting properties of the steel.

Relative cutting abilities (with the cutting ability of steel Grade P18 taken equal to unity) and red hardness values (i.e. the temperature of tempering for 4 hours upon which the steel hardness lowers to 58 *HRC*) of selected high-speed steels are given in Table 17.10.

Thus, a high red hardness and high cutting properties are mainly due to the dissolution of secondary carbides and alloying of the solid solution with the elements constituting these carbides. If however, the content of a carbide phase in as-annealed steel P18 is 25 per cent, only 10 per cent pass to the solution and 15 per cent remain as inclusions in the structure.

It cannot be said however that excess carbides are useless. Their positive role is in that they inhibit the growth of austenitic grains. Without primary carbides, a high temperature of hardening (1 200°C or higher) would form coarse-grained austenite and increase the brittleness. It is known, however, that most high-speed steels have a fine grain and porcelain-like lustreless fracture not typical of

Table 17.10. Cutting Ability[1] and Red Hardness of High-speed Steels

Steel Grade	Cutting ability	Red hardness, RH_{58}, °C	Steel Grade	Cutting ability	Red hardness, RH_{58}, °C	Steel Grade	Cutting ability	Red hardness, RH_{58}, °C
P18	1.0	620	P6M5	1.0	620	P9K10	1.15	640
P12	1.0	620	P9Ф5	1.05	625	P10K5Ф5	1.1	635
P9	1.0	620	P14Ф4	1.1	630	P18K5Ф2	1.1	640
P6M3	1.0	620	P18Ф2	1.0	630	P9M4K8	1.25	640

[1] Cutting speed for the same durability (cutting speed of steel Grade P18 is taken as unity).

brittle steels. Since steel P18 contains more carbides, it is superior to Grade P9 in being less sensitive to overheating.

Metallographic studies of high-speed steels can readily reveal the structural changes that occur in them on heating.

Figure 17.10*a* shows the microstructure of steel Grade P18 upon hardening from 1 240°C. As may be seen, the austenite is fine-granular and contains much of carbides. In Fig. 17.10*b*, the structure of the same steel is shown after hardening from 1 280°C, which is the optimum hardening temperature for that steel grade. Now it has a coarser austenitic grain and an appreciably lower quantity of carbides, which is an evidence that the austenite has been alloyed more heavily. Hardening from a higher temperature causes an appreciable

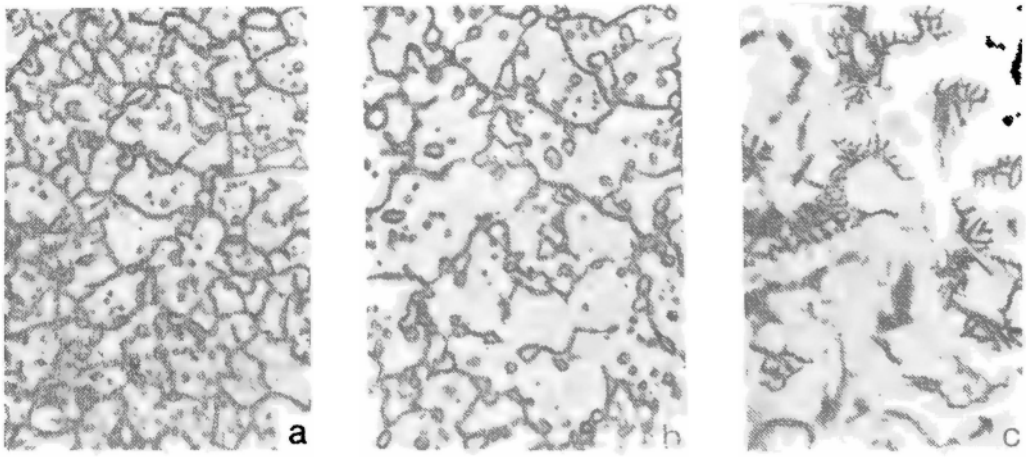

Fig. 17.10. Microstructures of steel P18. ×500. Hardening temperatures (*a*) 1 240°C (underheating); (*b*) 1 280°C (normal heating); (*c*) 1 340°C (overheating)

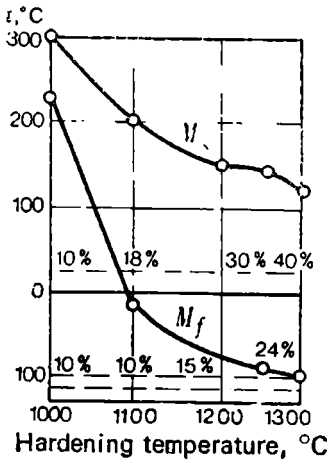

Fig. 17.11. Effect of hardening temperature on the temperature of the beginning and end of martensitic transformation and the quantity of retained austenite prior to (upper numbers) and upon (lower numbers) cooling in liquid oxygen (the author)

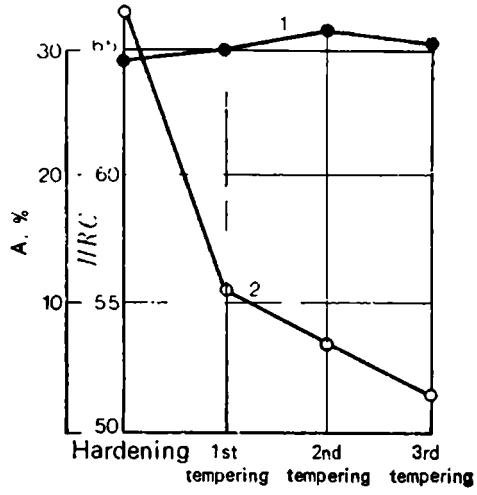

Fig. 17.12. *HRC* hardness (*1*) and the quantity of retained austenite (*2*) in steel P18 depending on the number of tempering stages. Hardening from 1 300°C, tempering at 560°C (the author)

growth of austenitic grain and the formation of a carbide network and in some cases may result in local melting and the appearance of the eutectic structural component (Fig. 17.10*c*).

As the hardening temperature increases, the austenite becomes richer in carbon and alloying elements which actively lower the martensitic point. As a result, the quantity of retained austenite increases (up to 30-35%), which is illustrated by Fig. 17.11. As may be seen, when the temperature of hardening is above 1 000°C, the temperature point of the end of martensitic transformation is below 0°C, so that cooling to sub-zero temperatures can produce a more complete transformation of retained austenite into martensite[1].

The tempering of hardened steel is mainly needed to decompose fully the retained austenite which otherwise might impair the cutting ability of tools.

Heating up to 500-550°C causes no substantial changes in hardened high-speed steel; a higher temperature (560-600°C) causes precipitation of carbides from the austenite and the latter transforms into martensite on subsequent cooling. This transformation, however, does not proceed to completion, but if the tempering operation at 560-580°C is repeated several times, the retained austenite can be transformed completely or almost completely into martensite (Fig. 17.12).

[1] This method is often used for the heat treatment of high-speed steel tools.

The phenomenon described is called *secondary hardening or secondary hardness*, since, as we already know, the formation of martensite is an essential moment in the hardening of steel. If the tempering temperature does not exceed 600°C, a repeated tempering operation will not lower hardness, but on the contrary, can even increase it somewhat compared to the as-hardened state (Fig. 17.12). Tempering at a temperature above 600°C would, however, give a lower hardness owing to decomposition of martensite and coagulation of carbides.

The microstructure of a steel as hardened and tempered should consist of fine acicular martensite and carbides (Fig. 17.13*a*). If the steel has not been tempered properly (Fig. 17.13*b*), residual austenite can also be found in the structure.

Having considered the transformations in high-speed steels, let us discuss their heat treatment (Fig. 17.14).

The hardening temperature should be as high as possible, but not above the temperature at which intensive grain growth or fusion begins. The optimum temperatures of hardening for selected high-speed steels are given in Table 17.11. For example, the optimum hardening temperature for steel Grade P18 is 1 270-1 290 C and for Grade P9, 1 220-1 240°C. Since the heat conductivity of steel is rather low, fast heating for hardening can cause cracking of tools and should therefore be avoided. It is advisable to employ preheating. The most popular method is two-stage preheating, respectively at 500-600°C and 830-860°C.

A long time of holding at the hardening temperature promotes dissolution of carbides and thus produces the same effect as an increase in the hardening temperature.

Quenching of high-speed steels should be done in oil. A slow cooling from the high hardening temperature (for instance, air cooling) might cause precipitation of carbides and impair the cutting properties of tools.

Stepwise cooling may be effective in diminishing hardening deformation.

Two methods can be recommended for the tempering of high-speed steels. The first (Fig. 17.14*a*) consists in that the hardened tools are tempered three times at 560°C for one hour every time. The quantity of retained austenite in the structure is 15 per cent after the first tempering stage, 3-5 per cent after the second, and only 1-2 per cent after the third. This method of tempering can raise the hardness up to 64-65 *HRC*. The formation of martensite on tempering occurs, as has been indicated earlier, during cooling from 150 to 20°C (the temperature ranges of the formation of martensite are shown by wavy lines in Fig. 17.14).

By another method of tempering (Fig. 17.14*b*), hardened tools are subjected to sub-zero treatment at —80°C. The cooling from room temperature to —80°C forms additionally 15-20 per cent

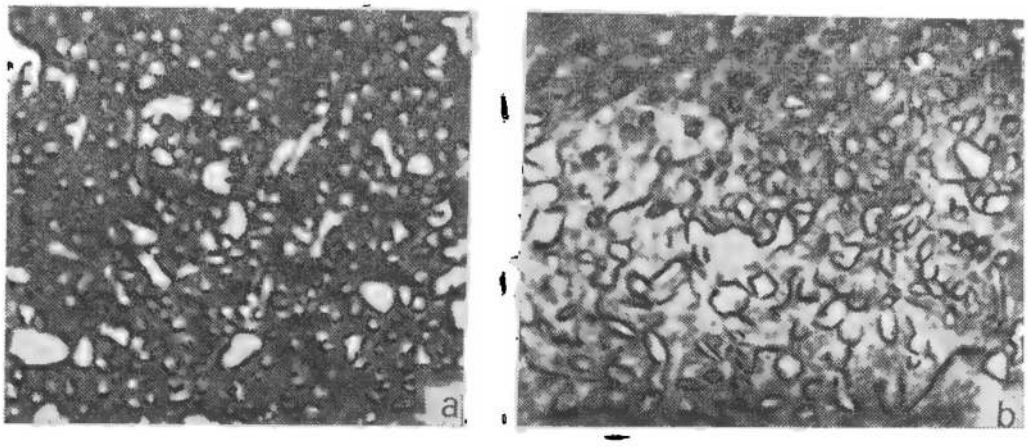

Fig. 17.13. Microstructure of high-speed steel as tempered

(*a*) well tempered steel, martensite + carbides. ×1 000; *b*) undertempered, martensite + + austenite + carbides. ×600

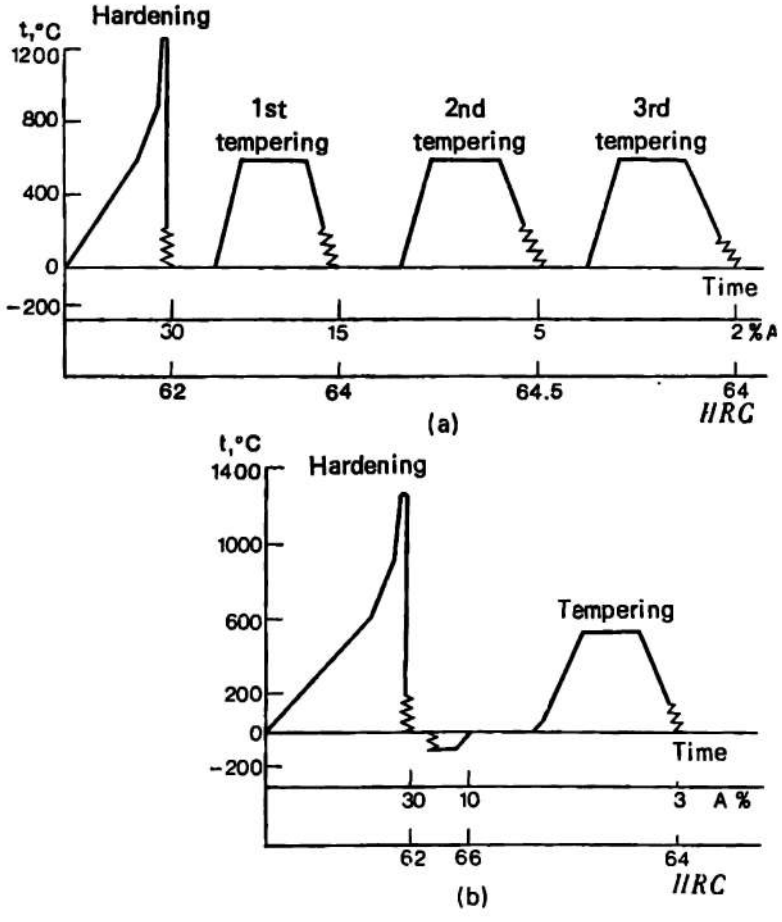

Fig. 17.14. Heat-treating conditions for high-speed steel tools

(*a*) without sub-zero treatment; (*b*) with sub-zero treatment

Table 17.11. Temperature Conditions of Heat Treatment for High-speed Tools

Steel Grade	Hardening			Tempering		
	temperature, °C	*HRC*	content of austenite, %	temperature, °C	number of tempering stages	*HRC*
P18	1 270-1 290	62-64	25	560	3	63-65
P12	1 240-1260	62-64	25	560	3	63-65
P9	1 220-1 240	62-64	30	560	3	63-65
P6M3	1 210-1 230	62-64	25	550	2-3	63-65
P6M5	1 210-1 230	62-64	25	550	2-3	63-65
P9Ф5	1 230-1 250	62-64	40	570	3	64-66
P14Ф4	1 240-1 260	62.5-64.5	35	570	3	64-66
P18Ф2	1 270-1 290	62-64	35	570	3	64-66
P9K10	1 220-1 240	62.5-64.5	30	570	2-3	64-66
P10K5Ф5	1 230-1 250	62.5-64.5	35	570	3	64-67
P18K5Ф2	1 270-1 290	62.5-64.5	30	570	3	64-66
P9M4K8	1 220-1 240	63-65	35	550	2-3	65-68

martensite in the structure (of the total volume of steel) and the quantity of retained austenite after this treatment is 10-15 per cent. This austenite transforms into martensite upon single-stage tempering at 560°C.

The temperature conditions for the heat treatment of high-speed steels are given in Table 17.11.

The cutting properties of some types of tool can be improved by low-temperature cyaniding: heat-treated (hardened and tempered) tools are additionally treated in molten cyan salts at 520-580°C for a short time. The procedure forms a very thin (a few micrometres) surface layer saturated with nitrogen and carbon, which increases substantially the wear resistance of the tools.

The corrosion resistance and cutting ability of tools can be improved by *steam treatment*, i.e. by heating the tools in the atmosphere of hot steam (the temperature is the same as for tempering). The procedure forms a thin (2-3.5 μm) film of magnetic iron oxide on the surface of tools, which prevents adhesion of chips and increases the corrosion resistance of the tool steel.

High-speed steel should be well annealed before being subjected to heat treatment.

This is commonly done by the isothermal annealing process, since it requires little time. The steel is heated for 1.5-2h at 860-900°C and then is cooled down to 700-750°C. The holding is required to let the austenitic transformation proceed to completion.

The hardness of steel as annealed should be 207-255 *HB*. Its structure is sorbite with inclusions of primary and secondary carbides (see Fig. 17.8*b*).

A special type of defect is often found in hardened high-speed steels if the prior annealing was done improperly: with an adequate hardness and the normal

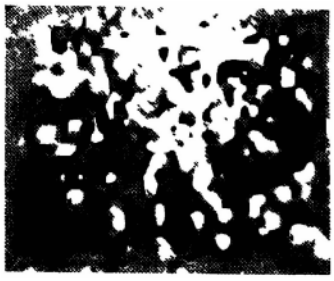

Fig. 17.15. Flaky fracture in high-speed steel

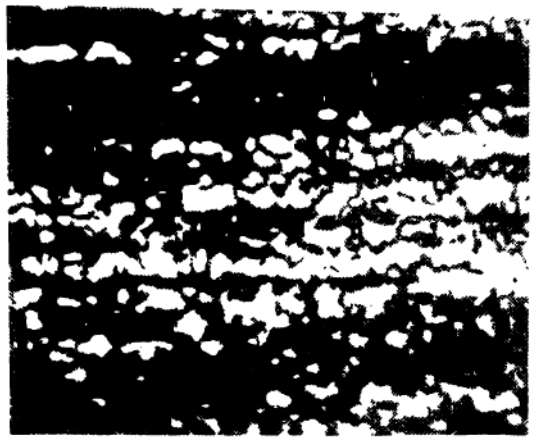

Fig. 17.16. Carbide segregation in high-speed steel. ×100

percentage of retained austenite in the structure, the steel turns out to be very brittle and its fracture, coarse-granular flaky (Fig. 17.15).

The quality of high-speed steel depends appreciably on the degree of forging deformation. With an insufficient forging deformation, the steel may be infected with *carbide segregation* (Fig. 17.16), i.e. its structure contains portions of the ledeburitic eutectic not destroyed by the forging deformation. A noticeable carbide segregation can impair the quality of high-speed steel (lower the durability and increase the brittleness of tools, etc.).

17.5. DIE STEELS

Plastic working of metals is done by means of various die tools (upper and lower dies, rolls, rollers, etc.), which deform the metal These tools are made of a special class of steel called die steels.

Die steels are separated into two large groups, respectively for deforming metal in a hot or a cold state, i.e. for hot and cold working. The conditions of operation of die steels in tools may be very diverse depending on the particular process of plastic working.

In hot die-forming, the hot metal is deformed between the approaching die pieces and fills in the inner face of the die (die impression). The working face of a die (die impression) is in contact with the hot metal being deformed, and therefore, a steel for hot-working dies should retain its high mechanical properties when heated. It is especially advantageous to have a high yield limit (elastic limit), since otherwise the die might be deformed by the high working pressure in the tool. In hammer dies, a high toughness of the die metal is also quite important to withstand working strokes. Wear resistance is of high importance in all cases, since it ensures that the die impression will not be distorted and the die will serve for a long time.

For press tools operating without impacts, a high wear resistance in a hot state is of great importance, while a high toughness is less essential. This is why hammer dies and press tools are made of different grades of steel.

Steels for making cold-forming dies must have a high hardness which ensures the resistance of the tool to abrasion; a high toughness is also essential, especially in punch dies.

Steels for hot-working dies must have the least sensitivity to local heating. If a steel is insufficiently tough (plastic), for instance, has not been annealed properly, local heating may cause cracking in it.

The steel in moulds for pressure die casting operates under even more severe conditions. The working face of the mould is heated by the molten metal and the inner portions are cooled by cooling water, which causes appreciable internal thermal stresses. A steel for making pressure moulds should also possess a high wear resistance, high mechanical properties in the heated state, and a high resistance to erosion by the molten metal.

Steels for making large-size dies should additionally possess a high hardenability. Further, steels for dies and punches of intricate shape should deform as little as possible during hardening.

In view of these numerous and diverse requirements imposed upon die steels, their grades are also very diverse, beginning from plain carbon steels and up to complex-alloyed steels.

Let us discuss separately the grades of die steels employed in cold and hot dies.

Tools for cold working of metal should have a high hardness (usually not less than 58 *HRC*). In many cases a high hardness (above 62 *HRC*) ensures a longer durability of tools. For that reason, the steels employed for the purpose contain not less than 1% C in the state of low-tempered martensite, i.e. after hardening and low-temperature tempering. The steels suitable for making these tools have been described in Secs. 17.1 and 17.2.

Steel Grades У10, У11 and У12 are used for making dies of small dimensions and simple shape; since their hardenability is not large, they can be used only for relatively light performance conditions (low deformation, low hardness of the worked material).

Dies of a more intricate shape or for heavier conditions of operation are made of oil-quenched alloy steels of an elevated hardenability, most often of Grade X (ШХ15).

Rolls of cold-rolling mills, which can be regarded as cold-working press tools, are made of chromium steels with 1 or 2% Cr (Grade 9X: 0.95-1.10% C, 1.4-1.7% Cr; Grade 9X2: 0.85-0.95% C, 1.7-2.1% Cr). Since the rolls are large in diameter, they are quenched in water and then tempered at a low temperature (100-120 C) so as to have the maximum hardness (64-66 *HRC*) in the surface layer (up to 10-15 mm deep). These and some other conditions (no overheating, uniform distribution of carbides, etc.) are essential for ensuring a high durability of rolls.

On the other hand, some cold-working tools of the impact type (marking punches, pneumatic hammers, chisels, etc.) should have a limited hardness (at a level of 52-58 *HRC* depending on tool type and operating conditions).

Plain carbon steels (Grades У7, У8, У9) can be used in tools for relatively light operating conditions with light strokes and small deformations (for in-

Table 17.12. Composition, Properties and Heat Treatment of Steels for Making Cold-forging Tools (GOST 5950—73)

Steel Grade	Content of elements, %				Hardening		Tempering	
	C	Si	Cr	W	temperature, °C	*HRC* (minimum value)	temperature, °C	*HRC*
4XC	0.35-0.45	1.2-1.6	1.3-1.6	—	880-890	47	240-270	51-52
6XC	0.60-0.70	0.6-1.0	1.0-1.3	—	840-860	56	240-270	52-53
4XB2C	0.35-0.44	0.6-0.9	1.0-1.3	2.0-2.5	860-900	53	240-270	50-52
5XB2C	0.45-0.54	0.5-0.8	1.0-1.3	2.0-2.5	860-900	55	240-270	51-53
							420-440	45-47
6XB2C	0.55-0.65	0.5-0.8	1.0-1.3	2.0-2.5	860-900	57	240-270	53-55
							420-440	46-48

Notes. 1. All these steels may contain 0.2-0.4% Mn, <0.3% Ni, and 0.03% S and P.
2. The hardness upon hardening is given as specified by GOST; that upon tempering, within a common range of variation.

stance, in hand punches, hand chisels, etc.). The desired hardness (58 *HRC*) is obtained by hardening and tempering at 250-350°C. Good results have been obtained by what is called 'gradient hardening', or *hardening with self-tempering* (see Sec. 11.7). The degree of heating in self-tempering is controlled by the time of quenching or by temper colours. These methods of heat treatment give a non-uniform hardness: high in the working portion and gradually decreasing in the non-working portion of a tool; this circumstance ensures a high durability of these tools. In pneumatic tools and other types of impact tool where a higher toughness is needed than in steels hardened by the gradient hardening, use is made of steels with a lower carbon content which are hardened to a hardness value of approximately 52 *HRC*. The compositions of some of the commoner die steels are given in Table 17.12. The table also indicates the principal conditions of heat treatment (hardening and tempering temperatures) and the hardness of steels as hardened. Naturally, these alloy steels are quenched in oil. The steels alloyed with silicon only have a lower hardenability than those containing tungsten; the latter refines the grain and increases the toughness of steel.

An increase in the carbon content makes a steel harder and more wear resistant, but lowers its toughness. Taking this in view, Cr-Si and Cr-W-Si steels can be made with a different carbon content.

High-chromium steels (12% Cr at 1-1.5% C), which possess a high wear resistance, elevated thermal stability, low deformability during heat treatment and some other valuable properties, have found a wide application for making cold-working dies and other tools for deforming metal in cold or relatively low-heated state (knurling dies and rollers, drawing dies, etc.). The compositions of some grades of die steel for cold-working tools are given in Table 17.13.

All high-chromium die steels contain usually 12% Cr (steel Grade Х6ВФ with 6% Cr will be discussed later) and a high percentage of carbon. This results in the formation of a large quantity of chromium carbides (Cr_7C_3). For instance, steel Grade Х12Ф1 as annealed contains 15-17 per cent of the carbide phase M_7C_3 and steel Grade Х12, 25-30 per cent (since the latter contains almost twice as much carbon).

Table 17.13. Compositions of Steels for Making Cold-forming Dies, % (GOST 5950—73)

Steel Grade	C	Cr	Mo	W	V
X12	2.0-2.3	11.5-13.0	—	—	—
X12BM	2.0-2.2	11.0-12.5	0.6-0.9	0.5-0.8	0.15-0.3
X12M	1.45-1.7	11.0-12.5	0.4-0.6	—	0.15-0.3
X12Ф1	1.2-1.45	11.0-12.5	—	—	0.7-0.9
X6BФ	1.05-1.14	5.5-7.0	—	1.1-1.5	0.5-0.7
6X6B3MФC (55X6B3CMФ)	0.5-0.6	5.5-6.5	0.6-0.9	2.5-3.2	0.5-0.8
80X4B3M3Ф2	0.75-0.85	3.5-4.5	2.5-3.0	2.5-3.2	1.9-2.5
7XГ2BM	0.68-0.76	1.5-1.8	0.5-0.8	0.5-0.9	0.1-0.25

Note. All these steels may contain not more than 0.4% Si, 0.35% Mn, 0.35% Ni, and 0.03% P and S.

The high content of the excess carbide phase (with any method of heat treatment) is exactly what makes the steel wear resistant. These carbides are capable of passing partially into the solution, especially at a high temperature of heating for hardening. This circumstance is made use of for changing the properties of a steel and its behaviour in heat treatment by varying the temperature of hardening.

The steels of the type X12 are similar to high-speed steels in their nature and undergo the same transformations.

High-chromium steels belong to the ledeburitic class, since the primary carbides precipitated during solidification form a eutectic (ledeburite) in as-cast steel. This eutectic is however destroyed during forging, so that the structure of the steel as annealed upon forging should consist of sorbite-like pearlite with inclusions of secondary carbides.

The diagram in Fig. 17.17 shows the effect of hardening temperature on the hardness (*HRC*) and the quantity of austenite (*A* %) in steel Grade X12Ф1. Hardness first increases with the hardening temperature, which can be explained by the fact that chromium carbides are poorly soluble in austenite, so that underalloyed martensite forms on hardening from 850-900°C. The highest hardness in steel X12Ф1 is obtained on hardening from 1 075°C. A higher temperature of hardening can give a lower hardness owing to a greater dissolution of chromium carbides and an increased amount of retained austenite.

Steel type X12 can be hardened to a desired high hardness by quenching in oil from a high temperature (1 150°C), and therefore, by retaining more austenite in the structure. The retained austenite can then be decomposed by sub-zero treatment and tempering to obtain high hardness (above 60 *HRC*). This method of heat treatment for secondary hardness, which was first applied to high-speed steels, is now used to advantage with high-chromium steels. A more common method employed with steel type X12 is, however, to harden from the temperature of maximum hardness (1 050-1075°C) and temper at a low temperature (at 150-180°C). The hardness is the same in both instances (61-63 *HRC*), but the former method gives a higher red hardness and the latter, a higher strength.

The recommended conditions of heat treatment for steel Grades X12Ф1 and X12M (the two grades are practically equivalent), the properties thus obtained,

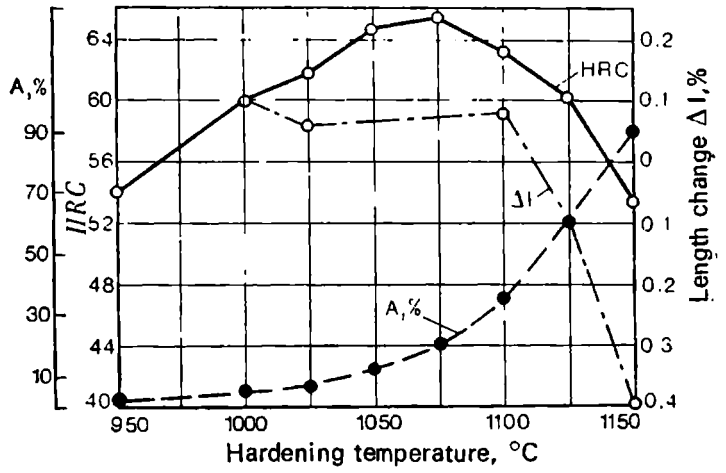

Fig. 17.17. Effect of hardening temperature on hardness, quantity of retained austenite and length variation (Δl) in steel X12Ф1 (the author)

and certain data on the structure (the quantity of retained austenite) are given in Table 17.14.

Since the quantity of retained austenite in steel type X12 can vary within very wide limits (from almost zero to 100%), the volume changes during hardening can naturally vary appreciably. Hardening to martensite increases the volume of steel (relative to the initial volume), while hardening to austenite diminishes it (see curve Δl in Fig. 17.17). At a definite temperature, the austenite-to-martensite ratio in the structure is such that the volume of as-hardened steel is exactly equal to its volume in the initial state. As follows from the graph in Fig. 17.17, this occurs at $\Delta l = 0$, i.e. when hardening has been done from 1 120°C, the structure contains roughly 40 per cent of retained austenite, and the hardness is 58 *HRC*. Usually, however, various deviations from the specified temperature of hardening, cooling conditions etc., result in that the dimensions of a hardened die are not exactly equal to its dimensions in the initial state.

Table 17.14. Heat Treatment Conditions for Steel Grade X12Ф1 (X12M)

Heat treatment mode	Temperature, °C	Quenching medium	*HRC* upon hardening	Quantity of austenite, %	Tempering temperature, °C	Number of tempering stages	*HRC* upon tempering
I	1 070±10	Oil (saltpetre)	62-64	20-25	160	1	62-64
II	1 070±10	Ditto	62-64	20-25	200	1	58-60
III	1 170±10	Oil (saltpetre)+ +freezing at −70°C	151-153	30-35	520	2-3	60-62
IV	1 120±10	Oil (saltpetre)	57-59	35-45	Thermal finishing		57-59

Note. I—common heat treatment mode; II—employed when treatment by mode I cannot ensure the required toughness; III—for cutting tools when high wear resistance is essential; IV—employed when dimensional stability is required.

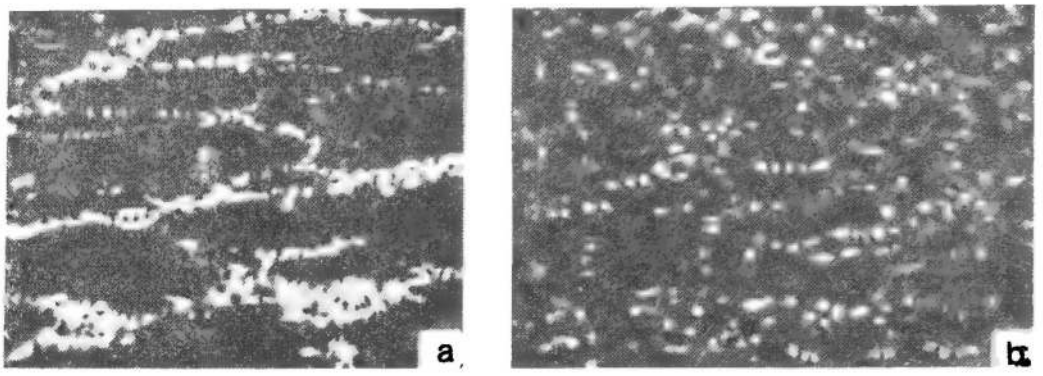

Fig. 17.18. Microstructures of steels. ×100
(*a*) X12; (*b*) X6ВФ

If a die has contracted, i.e. its dimensions have decreased, tempering at 520°C is assigned. The operation causes part of the retained austenite to transform into martensite, which will increase the dimensions of the die. On the other hand, if a die has grown in size during hardening, it is tempered at a temperature of 350°C to restore its dimensions. At this temperature, the retained austenite remains unchanged in the structure, whereas the tetragonal martensite transforms into temper martensite.

The tempering operation described is called *thermal finishing* and allows the dimensions of large dies to be controlled with an accuracy of ± 0.1 mm.

Steels X12Ф1, X12M and the like deform only slightly during hardening, so that hardening deformations can be reduced practically to zero by thermal finishing. This is why these steels can be recommended for tools of intricate shape in which hardening deformation is inadmissible.

An essential shortcoming of steel X12 is its reduced mechanical strength, which is due to the presence of a large amount of carbide phase in the structure. Since the content of this phase is greater at a higher content of carbon in steel, steel X12 (with 2.0-2.3% C) is only used for less critical purposes and in tools of simple shape.

The distribution of carbide phase is of great importance for high-speed steels and those of type X12. Lineage structure of carbides, carbide clusters and all other defects associated with what is called carbide segregation can impair appreciably the strength of steel. The quality of steel can be improved by a large forging deformation which diminishes the cross-section of metal pieces (blanks, rods) and disintegrates carbide accumulations (Fig. 17.18*a* and *b*). Heavy forging is therefore advisable for large-size dies in all cases. A heavy forging deformation in these cases is achieved by alternate upsetting and drawing. Even these radical measures, however, are not always capable of eliminating the carbide segregation as desired.

A steel of the considered class but with a lower content of carbon and chromium and less sensitive to carbide segregation is represented in Table 17.13 by Grade X6ВФ. It contains less carbides than steel type X12 (12-14% of M_7C_3 carbide in steel X6ВФ as annealed, compared to 15-17% in X12Ф1 and 25-30% in X12) and is relatively less liable to carbide segregation (Fig. 17.18*b*).

Steel Grade X6ВФ behaves in heat treatment in the same manner as steels type X12, though an elevated temperature of hardening does not give as strong dissolution of carbide phase as in type X12 (Fig. 17.19). This makes it possible to harden this steel from 1 000° ± 10°C (to obtain the maximum hardness). Upon this hardening, roughly 8 per cent of carbides (of the total of 12%) passes

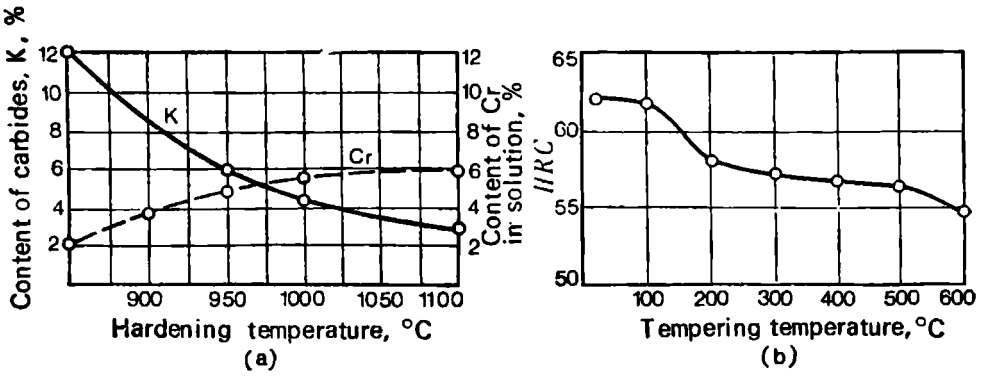

Fig. 17.19. Effect of heat treatment on the structure and properties of steel X6BΦ (the author)

(*a*) effect of hardening temperature; (*b*) effect of tempering temperature

to the solution and the martensite contains approximately 5% Cr in the solution.

This martensite is quite resistant against tempering (Fig. 17.19*b*). Tempering at 200°C lowers the hardness to 58 *HRC* and a further increase in temperature (up to 500-525°C) has only a slight reducing effect on hardness (from 58 to 55-56 *HRC*). Since the strength and toughness of the metal also vary only slightly in that range of tempering temperatures (this pattern of variation of properties is also typical of steels type X12), steel Grade X6BΦ is usually tempered either at 150°C (to preserve the high hardness) or at 200°C (to increase somewhat the toughness).

It follows from the foregoing that the heat treatment conditions and applications of steels X6BΦ and X12Φ1 are quite similar, but the former has a higher strength and lower wear resistance (owing to a lower percentage of carbide phase).

Let us now consider the steels employed for making hot-working dies. The metal of a hot-working die should possess a specific complex of properties which will be discussed below.

Heat resistance. The metal of hot-working dies should possess a high yield limit and a high wear resistance at the high working temperatures. This is needed to slow down the processes of wear and deformation of the elements of die impression, which are heated up at contact with hot metal.

Red hardness. The high heat resistance of the die metal should not decrease during a long time of heating at the working temperature, i.e. the die metal should have an appropriate resistance to tempering.

Thermal stability. Alternating cycles of heating and cooling of the die surface during operation, and therefore, alternating expansion and contraction of the surface layers of the metal can result in hot cracking. The die metal must possess a high resistance to hot cracking, which can also be called thermal stability, or thermal fatigue resistance.

Toughness. During the hot-working operations, the die metal may suffer from impacts and should therefore possess an adequate toughness; this is especially important for hammer dies in which an elevated toughness is often formed at the expense of heat resistance.

Hardenability. Many dies are quite large in size (for instance, cubes of hammer dies may be as large as 500 × 500 × 1 000 mm), so that the die metal should have an appropriate hardenability in order to obtain the desired properties, in particular, a high toughness all over the cross-section.

Temper brittleness. Since temper brittleness in large-size dies cannot be eliminated by fast cooling, the die metal should be as much as possible insensitive to this defect.

Adherence. At appreciable pressures acting in a die, hot metal can adhere to the die metal (the phenomenon of *adhesion*) and gradually deteriorate the surface of the die. The deteriorating effect is stronger with a stronger adhesion between the metal being worked and the die metal, so that the adhesive effect should be minimized where possible.

Dies for operation under light conditions[1] are made of carbon steels with 0.6 to 1.0 per cent carbon, i.e. Grades У7, У8 and У9; among them, Grade У7 is most popular for making dies.

It should be noted however that carbon steels cannot ensure the desired durability of dies and are therefore poorly applicable in modern high-intensity die-forging.

Dies for heavier performance conditions are made of alloy steels[2].

The compositions of selected alloy steels for hammer dies are given in Table 17.15.

The most typical and popular and probably the best among the steels given in the table is Grade 5ХНМ, the other grades in which nickel (or molybdenum) is replaced by other elements are of inferior quality and serve only as substitutes for Grade 5ХНМ.

The properties of steel Grade 5ХНМ can be illustrated by the graph in Fig. 17.20. The curves show the effect of tempering temperature on the steel properties and also the effect of test temperature for the steel as hardened and tempered at 550°C (i.e. after the heat treatment specified for dies made of this steel, see for more detail later in this section). As may be seen, the strength of the steel diminishes with increasing temperature of tempering, while the ductility and toughness increase; an increase in the test temperature acts in the same sense.

The mechanical properties of die steels at room temperature (upon hardening and tempering at 550°C) are typically as follows: σ_t = 120-130 kgf/mm², δ =

[1] Light conditions include die-forging with a light pressure on the die surface, for instance, with low deformations, and die-forging of soft and plastic alloys.

[2] Heavy conditions imply high-productive die-forging, die-forging of large pieces, and also cases when the die impression has an appreciable depth and is of an intricate shape.

Table 17.15. Compositions of Steels for Making Hammer Dies, % (GOST 5950—73)

Steel Grade	C	Mn	Si	Cr	Ni	Mo, W, Ti
5XHM	0.5-0.6	0.5-0.8	0.15-0.35	0.5-0.8	1.4-1.8	0.15-0.30Mo
5XГM	0.5-0.6	1.2-1.6	0.25-0.65	0.6-0.9	—	0.15-0.30Mo
5XHCB	0.5-0.6	0.3-0.6	0.6-0.9	1.3-1.6	0.8-1.2	0.4-0.6W
5XHT	0.5-0.6	0.5-0.8	0.15-0.35	0.9-1.25	1.4-1.8	0.08-0.15Ti

= 10-13 per cent; ψ = 40-45 per cent, and a_{n_I} = 4-5 kgf m/cm². These values are exhibited by all the steels given in Table 17.15 except for Grades 5XГM and 5XHT.

Steel Grade 5XГM has a reduced ductility (ψ = 30%) and a lower toughness (a_{n_I} = 3-4 kgf m/cm²), which is a natural result of the replacement of nickel by manganese.

Steel Grade 5XHT which contains no elements (molybdenum or tungsten) that might retard the tempering process, softens more quickly on being tempered at 550°C and has a lower strength but a higher ductility.

The mechanical properties of hammer-die steels at 600°C are given in Table 17.16. Among the steels indicated in the table, Grade 5XHM exhibits the best complex of mechanical properties. Grades 5XГM and 5XHCB excel it in hot strength, but have a lower ductility (owing to the effect of manganese and silicon). Steel Grade 5XHT contains neither molybdenum nor tungsten (which might inhibit decomposition of martensite) and has a lower strength at 600°C.

As can be seen from the data of Table 17.17, temper brittleness develops in steel Grade 5XHT and does not in Grades 5XHM and 5XHCB (these two grades are alloyed with molybdenum or tungsten).

As regards their hardenability, these steels can be written in the following descending order: 5XHCB, 5XHM, and 5XHT.

Molybdenum and tungsten increase the thermal stability (evidently owing to grain-refining effect).

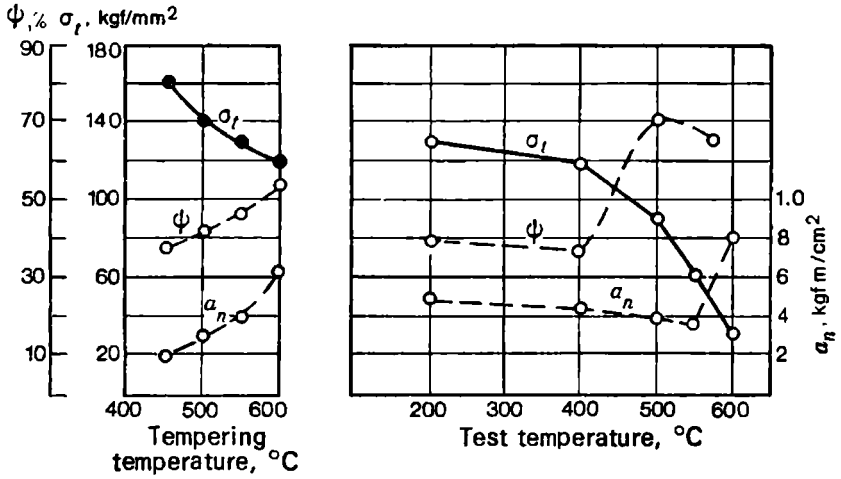

Fig. 17.20. Effect of tempering temperature and test temperature on the properties of steel 5XHM (M. V. Pridantsev)

Table 17.16. Mechanical Properties of Die Steels at 600°C

Steel Grade	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	ψ, %	a_{n_I}, kgf m/cm²
5XHM	35	25	65	8
5XГM	43	40	85	4
5XHCB	40	30	40	5
5XHT	25	20	90	8

Table 17.17. Impact Toughness of Die Steels upon Tempering at 500°C, kgf m/cm²

Steel Grade	Cooling after tempering		Relative embrittlement[1]
	quick	slow	
5XHM	7	6.2	0.8
5XHCB	5	4.7	0.3
5XHT	7	5.0	2

[1] Difference in impact toughness upon tempering with quick and slow cooling.

Steels of these grades are used for making die cubes (Fig. 17.21), i.e. large forgings of prismatic shape with the die impression cut in one of the faces. Upon forging, the cubes are annealed by the isothermal process[1].

The hardness of the steel if properly annealed should be 3.9-4.3 mm of Brinell indent.

The hardening and tempering of dies are very critical and complicated operations, mainly in view of the large size of dies.

Heating for hardening is done to the temperature 20-40°C above the Ac_3 point, as may be seen from Table 17.18.

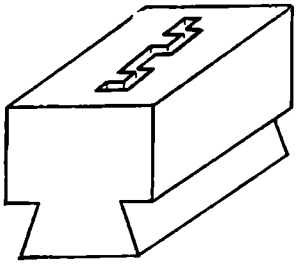

Fig. 17.21. Hammer die cubes

Cubes are placed into a hardening furnace at the temperature not above 650°C and held at that temperature for 1-2 hours. The temperature in the furnace is then gradually (for a few hours) raised to the specified value, after which a holding of a few hours is allowed[2]. The rate of heating and the holding time depend on the size and shape of dies, their number and the design of furnace (either electric or gas-fired). For instance, dies 250 × 400 × 500 mm in size should be heated in the furnace from 650° to 850°C for 7-8 h and held at 580°C for 1.5-2 h. With larger

[1] Austenitization at 850-880°C, cooling to 600-650°C, and a holding to full decomposition of austenite.

[2] Cubes less than 400 mm high can be placed into the furnace heated up to the hardening temperature.

Table 17.18. Critical Points of Hammer Die Steels and Adopted Temperatures of Heating for Hardening

Steel Grade	Critical points, °C			Temperature of heating for hardening, °C
	Ac_1	Ac_3	M_s	
5XHM	720	820	210	820-860
5XГM	700	800	220	820-840
5XHCB	760	800	235	860-880
5XHT	710	795	240	830-850

Table 17.19. Tempering Temperature and Hardness of Hammer Dies Made of Steel Grade 5XHM

Size (height) of die, mm	Tempering temperature, °C	Tempering time, h	Brinell hardness
250-300	480-510	9-11	387-444
300-400	520-540	11-15	363-387
400-600	550-580	15-22	302-341

dies (say, 500 × 800 × 1 000 mm), the time of heating increases to 20 h and the holding time, to 4-5 h.

In view of the high temperatures and long holding time, special measures should be taken to prevent oxidation and decarbonization of the die surface (this is done by using special fillers and pastes). Heated dies are quenched in oil. The best results are obtained by interrupted hardening.

Just after quenching, as soon as the dies have been cooled to 100-150°C, they can be transferred into a tempering furnace.

The tempering conditions to form the desired working hardness are selected from the experimental data on the durability of dies tempered at different temperatures. As a rule, it is of advantage that smaller dies have a higher hardness. The recommended temperatures of tempering and the respective hardness values obtained are given in Table 17.19.

Naturally, the holding time in tempering is longer with larger dies (since through heating is essential). The shanks of dies are additionally tempered at a higher temperature (approximately by 100°C higher than the tempering temperature for the dies) so as to reduce their hardness by 60-90 *HB* numbers as compared to the hardness of the dies.

Press tools and dies for horizontal forging machines and presses are made of more heavily alloyed steels in order to have a higher heat resistance at the expense of ductility.

The compositions of steels for dies of horizontal forging machines and presses are given in Table 17.20.

High-speed steels could be principally suitable for this purpose were it not for their insufficient ductility.

Table 17.20. Compositions of Steels for Dies of Horizontal Forging Machines and Presses, % (GOST 5950—73)

Steel Grade	C	Mn	Si	Cr	W	Mo	V
3X2B8	0.3-0.4	0.15-0.4	0.15-0.40	2.2-2.7	7.5-9.0	—	0.2-0.5
4X5B2ФC (ЭИ958)	0.35-0.45	0.15-0.5	0.8-1.2	4.5-5.5	2.6-2.4	—	0.8-1.2
4X2B5ФM (ЭИ959)	0.35-0.45	0.15-0.4	0.15-0.35	2.0-3.0	4.5-5.5	0.6-1.0	0.6-1.0
4X3BФ2M2 (ЭП1)	0.35-0.45	0.3-0.5	0.15-0.35	3.0-3.7	2.0-2.7	2.0-2.5	1.5-2.0

The steels given in Table 17.20 are similar to high-speed steels (for instance, Grade 3X2B8 is very like Grade P9), but have a lower carbon content, and therefore, a higher ductility.

Grade 3X2B8 is the most popular in the group. Steel Grade 4X3BФ2M2 has shown an elevated durability in performance and Grade 4X5B2ФC, the same durability as Grade 3X2B8.

Steel Grade 3X2B8 as annealed contains around 12% M_6C carbide. Full dissolution of this carbide occurs at 1 200°C. The hardening of the steel is done from 1 100°C, with 7 per cent of the carbides passing to the solution and 5 per cent being retained as excess carbides. In that case the solid solution contains around 6% W, 2% Cr, 0.2% V, and 0.15% C. The structure of the steel as hardened from 1 100°C is martensite with a small amount of austenite and excess carbides; its hardness is 49-51 *HRC* and strength σ_t = 160 kgf/mm².

The strength and hardness of steel Grade 3X2B8 and the other steels in this group vary only slightly on tempering below 600-650°C (as in high-speed steels). This is indicative of the high red hardness of these steels (Fig. 17.22*a*), which is due to alloying with tungsten and molybdenum, the elements that form M_6C carbides coagulating only at temperatures above 600°C. This is why these steels have higher values of strength and hardness at elevated temperatures (up to 600-650°C, see Fig. 17.22*b*).

The mechanical properties of selected steels for press tools at elevated temperatures can be characterized by the values given in Table 17.21.

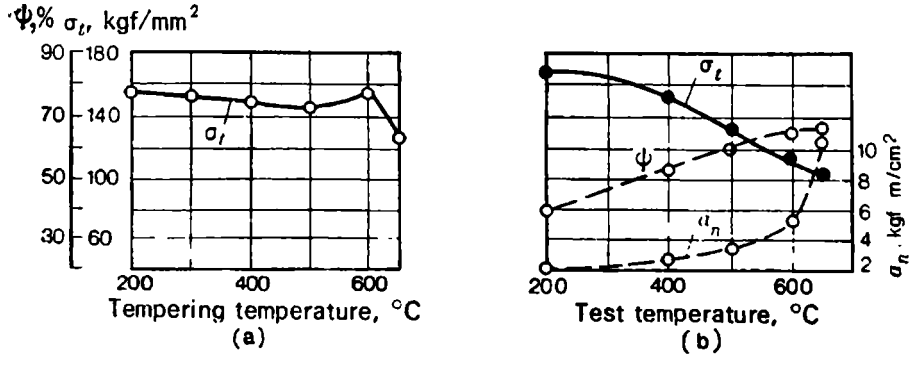

Fig. 17.22. Effect of tempering and test temperature on the properties of steel 3X2B8 (the author)

Table 17.21. Mechanical Properties of Steels for Press Tools (at 600°C)

Steel Grade	Temperature of heat treatment, °C		σ_t, kgf/mm²	ψ, %	a_{n_I}, kgf m/cm²	*HB*
	hardening	tempering				
3X2B8	1 100	600	110	50	4.5	300
4X5B2ФC	1 050	550	115	45	5.0	345
4X2B5ФM	1 050	550	120	40	3.0	360
4X3B2Ф2M2	1 100	600	110	35	4.0	300

Note. Steel Grades 4X5B2ФC and 4X2B5ФM have a higher strength due to a lower temperature of tempering.

It should not be thought that all elements of press tools are made only of the steels given in Table 17.21 or of like grades.

Dies and piercing and shaping punches of small length and large diameter, which operate at lower temperatures and pressures than other elements of press tools, are often manufactured of steel Grade 5XHM described earlier or of structural steel 30XГC.

Upper and lower dies for operation at high pressures and temperatures should be made of steel 3X2B8 or like grades. If impacts are likely to appear in die performance, steel 3X2B8 should be replaced with type 5XHM or 4X5B2ФC; the last grade has a higher toughness than 3X2B8 and a higher red hardness than 5XHM.

Therefore, the recommended steel grades for press tools are as follows:

(1) Grade 3X2B8 (see Table 17.20) for elements operating under especially high thermal loads;

(2) type 5XHM (Table 17.15) for elements subjected to impacts at relatively moderate thermal loads;

(3) Grade 4X5B2ФC for elements subjected to relatively high working temperatures and dynamic loads;

(4) structural steels type 30XГC or 40XH for die elements subjected to appreciable mechanical loads and low heating (up to 300°C).

The heat treatment of die elements of horizontal forging machines and presses (dies, punches, etc.) made of steel 3X2B8 or the like consists in hardening (oil quenching) and tempering. The main conditions of heat treatment for these steels are given in Table 17.22.

Dies operating at moderate temperatures of heating (400-500°C) can also be made of steel Grade 7X3 (0.6-0.75% C, 3.2-3.8% Cr, other elements in usual proportions). It has a higher wear resistance owing to a higher carbon content, but appreciably lower values of toughness and red hardness than grades 3X2B8 and 5XHM.

The temperature conditions in moulds for pressure die casting are similar to those of hot-working dies, so that pressure die casting moulds are made of the same grades of steel: 3X2B8 in elements operating at high thermal loads and simpler grades (7X3, 30XГC and even carbon steels 40 and У7) in elements operating under lower temperatures. Stainless steels of the type of 3X13, which will be discussed later in the book, are also used for the purpose.

Table 17.22. Heat Treatment Conditions for Steels of Press Tools

Steel Grade	Annealing		Hardening		Tempering	
	temperature, °C	*HB*	temperature, °C	*HRC*	temperature, °C	*HRC*
3Х2В8	750-780	187-220	1 050-1 100	48-50	600-620	38-44
4Х5В2ФС	840-880	207-229	1 020-1 060	—	580-620	44-50
4Х2В5ФМ	840-880	207-229	1 050-1 100	—	600-650	44-50
4Х3В2М2Ф	860-890	207-229	1 050-1 100	51-53	600-620	38-42

17.6. HARD ALLOYS

As can be seen from the diagram in Fig. 17.5, the working temperature for cutting tools made of hard alloys can be as high as 800 to 1 000°C, whereas for high-speed steel cutting tools temperatures above 700°C are inadmissible.

Therefore, hard-alloy cutting tools can operate at higher cutting speeds than high-speed steel tools.

This is why hard tools are now used extensively for metal cutting at high speeds.

Hard alloys belong to metal-ceramic alloys. For manufacture of hard alloys, powders of tungsten and titanium carbides are mixed with a binder (usually cobalt), pressed in pressure moulds to the desired shape, and sintered at a high temperature (1 500-2 000°C). The final products are not perfectly dense and pores in them occupy a volume of up to 5 per cent.

Since hard alloys are composed of 90-95 per cent carbides (the remainder being cobalt binder), i.e. substances of exceptionally high hardness, the hardness of sintered products is very high and they do not lend themselves to machining (except for grinding). Hard-alloy tools are usually of the composite type, i.e. a hard-alloy cutting plate is attached to a holder made of a common structural or tool steel.

Many cutting tools (milling cutters, drills, etc.) for high-productive machining are now made by this method.

Being very hard, hard alloys have a high brittleness and low resistance to tensile stresses. This shortcoming can be eliminated, though not completely, by properly selecting the shape of tools and the cutting conditions. Hard-alloy tools cannot withstand impact loads.

Table 17.23. Properties (Guaranteed) of Selected Hard Alloys

Alloy group	Alloy Grade	Composition,[1] %			Bending strength, kgf/mm²	Density, g/cm³	*HRA*
		WC	TiC	Co			
BK	BK2	98	—	2	1 000	15.0-15.4	90
	BK3	97	—	3	1 000	14.9-15.3	89
	BK6	94	—	6	1 200	14.6-15.0	88
	BK8	92	—	8	1 300	14.4-14.8	87.5
BTK	T5K10	85	5	10	1 150	12.3-13.2	88.5
	T14K8	78	14	8	1 150	11.2-12.0	89.5
	T15K6	79	15	6	1 100	11.0-11.7	90
TK	T30K6	66	30	4	900	9.5-9.8	92
	T60K6	36	60	6	750	6.5-7.0	90

[1] In the initial charge (the ratio of the mass of powders before sintering), but this does not characterize the phase ratio in a sintered alloy.

The compositions and some properties of selected standardized hard alloys are given in Table 17.23.

Modern hard alloys can be separated into three groups as regards their structure and the nature of carbide phases.

The first group (called BK alloys) includes single-carbide hard alloys which are composed of tungsten carbide. The alloys in the group are grades (BK3, BK6, BK8, BK10) according to the content of cobalt (3% Co in BK3, 6% Co in BK6, etc.). Hard alloys more rich in cobalt have a lower hardness and soften at a lower temperature, but are less brittle.

These circumstances should be considered when selecting a hard alloy for a particular application.

The structure of a single-carbide alloy from the BK group is shown in Fig. 17.23. Bright angular grains are crystals of WC carbide. Cobalt binder fills in the spaces between grain boundaries and cannot be revealed clearly by optical microscopy of etched sections. Dark portions in the figure are pores.

Tungsten carbide (WC) can dissolve almost no titanium, whereas titanium carbide (TiC) behaves in a different way. According to Ya. S. Umansky et al., titanium carbide can dissolve up to 70% W or, at a high temperature, up to 90%.

The constitutional diagram of a carbide system[1] is shown schematically in Fig. 17.24.

The second group of hard alloys includes two-carbide alloys (group BTK) and can be typically represented by T15K6 hard alloy. The powder mixture before sintering consists of 15 per cent titanium carbide and 79 per cent tungsten carbide. Owing to diffusion and dissolution of tungsten and carbon in titanium carbide, the final structure on sintering contains more than 50 per

[1] Strictly speaking, this is a pseudo-binary section through the ternary W-Ti-C system from 100% WC to 100% TiC.

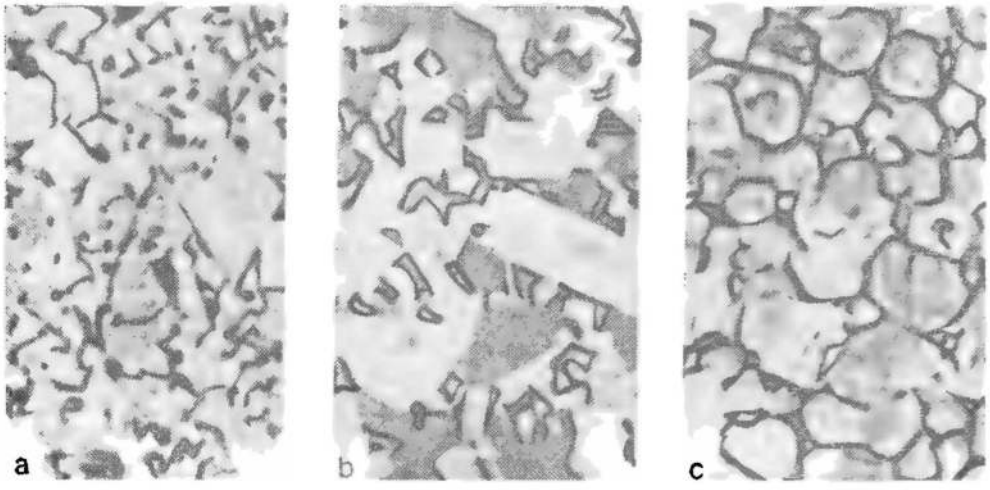

Fig. 17.23. Microstructures of hard alloys. ×100
(*a*) BK3; (*b*) T15K6; (*c*) T30K4

cent titanium carbide (Ti, W)C (large dark carbide particles in Fig. 17.23*b*). As may be seen from the constitutional diagram, the vertical corresponding to T15K6 alloy (i.e. when the initial mixture contains 15% titanium carbide) lies in the two-phase region; the same is true of T5K10 alloy which contains 5 per cent titanium carbide before sintering.

The third group (TK) includes single-carbide alloys T30K4 and T60K6 containing (Ti, W)C carbide. With such a high content of titanium carbide in the mixture (respectively 30 and 60%), all the tungsten present is dissolved in it. The verticals corresponding to these alloys lie in the single-phase region

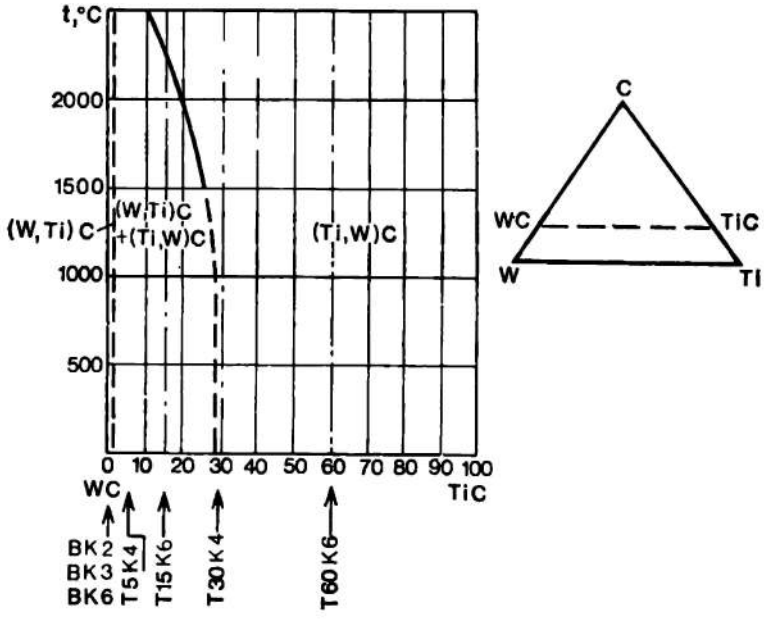

Fig. 17.24. Pseudo-binary section through W-Ti-C ternary system

of the solid solution based on titanium carbide (Fig. 17.24). The structure of these alloys consists of rounded-off grains of (Ti, W)C carbide (Fig. 17.23c).

Titanium carbide is harder and more brittle than tungsten carbide. Experience shows that group ВТК alloys are more suitable for machining steel and ВК alloys, for machining brittle materials. Group ТК alloys are employed in the processing of rocks and in the drilling of petroleum wells.

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Chapter 18

SCALE-RESISTING AND HEAT-RESISTING STEELS AND ALLOYS

Scale-resisting steels and alloys are those which can operate in slightly stressed or non-stressed state in hot gaseous media (at temperatures above 550°C) without chemical deterioration of the surface.

Heat-resisting steels and alloys are those which can retain their high mechanical properties at elevated temperatures.

High pressures and stresses and elevated temperatures are employed increasingly in modern engineering.

For instance, in 1920's steam boilers operated at steam temperatures up to 350°C and pressures of 17.5 at and consumed 0.7 kg of coal to produce 1 kW h of electric energy. In 1940's, the temperature of steam was raised to 400°C and the pressure, to 80-100 at, and coal consumption dropped down to 0.5 kg per kW h. In modern steam power plants which operate at supercritical steam parameters (580°C and 300 at), the consumption of coal is only 0.3 kg kW h.

It has been established that metals behave at elevated temperatures (even at 300-350°C) not in the same way as at normal temperatures.

It is therefore natural that metallurgists pay much attention to scale-resisting and heat-resisting steels and special alloys intended for operation at elevated temperatures.

18.1. SCALE RESISTANCE. SCALE-RESISTING ALLOYS

Scale resistance is the resistance of a metal to oxidation at elevated temperatures.

How does oxidation take place? The initial stage of oxidation of steel is a purely chemical process. As the oxidation proceeds, it becomes a complex process involving the diffusion of atoms of oxygen and metal through a multi-phase oxidized layer, as well as chemical combination of oxygen and metal. If the oxide film is dense, the rate of growth of the scale is determined by the rate of diffusion of atoms through it, which in turn depends on temperature and the structure of the oxide film.

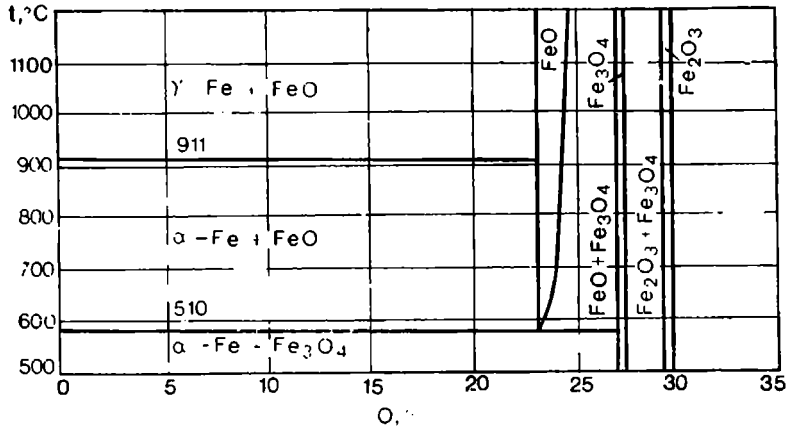

Fig. 18.1. Fe-O constitutional diagram

Iron can form a number of compounds with oxygen. FeO (wustite), Fe_3O_4 (magnetite), and Fe_2O_3 (haematite). As has been noted, the structure of a diffusion layer corresponds to an isothermal section through the corresponding constitutional diagram (Fig. 18.1) at the temperature of diffusion.

At temperatures below the eutectoid line (570°C), an oxidized layer consists of two oxide zones: Fe_2O_3 and Fe_3O_4. These oxides have a complicated crystal structure and the rate of diffusion in them is low.

At temperatures above 570°C, the structure of the scale is composed of three oxides: Fe_2O_3, Fe_3O_4 and FeO, the last oxide forming the main layer in the scale. The rate of oxidation increases on passage through the eutectoid line (570°C). This is due to a quicker diffusion of atoms (Fig. 18.2) through the simpler crystal lattice of wustite which crystallizes, as interstitial phases do, with a deficiency in non-metallic atoms (oxygen).

The scale resistance of steels is increased by alloying them with elements that can favourably change the composition and structure of scale. For instance, if a steel has been alloyed with proper amounts of chromium, aluminium or silicon, i.e. the elements which have a greater affinity for oxygen than iron, oxidation will result in the formation of dense oxides Cr_2O_3, Al_2O_3 or SiO_2 which offer a greater resistance to diffusion. A thin film of these oxides inhibits further oxidation.

The scale resistance of a steel, and therefore, the temperature at which the steel can be scale-resisting, increases with a greater content of chromium, aluminium or silicon. The lowest content of chromium to ensure scale resistance at various temperatures may be found in Fig. 18.3. To have an appropriate scale resistance at 900°C, an alloy (steel) should contain at least 10% Cr, and for operation at 1 100°C, not less than 20-25%.

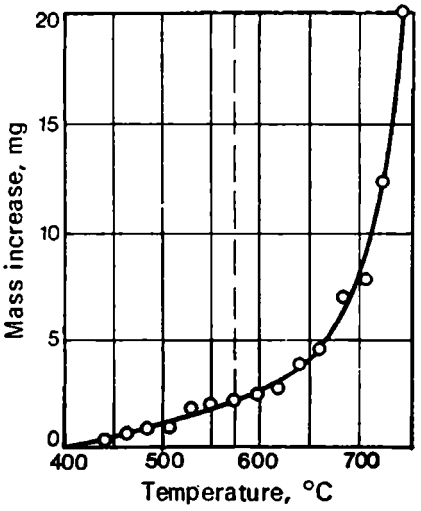

Fig. 18.2 Effect of temperature on the oxidation rate of iron (V. I. Arkharov)

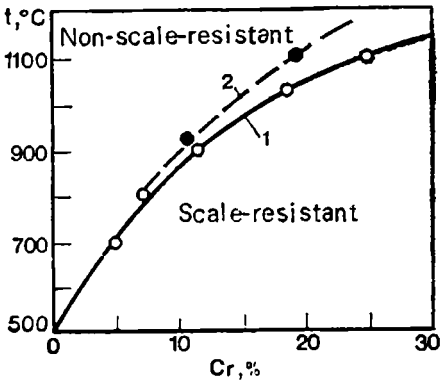

Fig. 18.3. Effect of chromium on the scale resistance of steels
1 — ferritic steels; *2* — austenitic steels

It is important to note that the scale resistance, which depends substantially on the composition of a steel or alloy, is independent of the structure of that alloy, i.e. it is a structure-insensitive property. For instance, as may be seen from Fig. 18.3, the scale resistance of ferritic (alloyed only with Cr) and austenitic alloys (Cr-Ni alloys) is practically the same.

The compositions of selected scale-resisting steels and alloys are given in Table 18.1. The working temperature indicated in the table is the temperature above which an alloy should not be heated in operation; otherwise quick oxidation is inevitable. Since alloying is expensive, it is essential to determine accurately the temperature conditions in each particular case of application and select accordingly the most appropriate steel grade from Table 18.1 or from other reference tables.

18.2. HEAT RESISTANCE

Heat resistance is the ability of a material to withstand mechanical loads at elevated temperatures.

The stress that can cause failure of a metal at elevated temperatures depends appreciably on the time of application of the load. The metal can withstand a high stress with a short time of load application and a lower stress if the load acts for a long time.

On the other hand, for a given time of load application, the failure stress is lower at a higher temperature. Therefore, the strength of metals at elevated temperatures is determined in the general case by two factors: temperature and time.

Table 18.1. Composition and Applications of Selected Refractory Steels (GOST 5632-72)

Steel Grade	Scale resistance, [1] °C	Content of elements, %						Applications
		C	Si	Mn	Cr	Ni	other elements	
		maximum values						
12X17	900	0.12	0.8	0.8	16.0-18.0	—	—	Sheets, rods
15X25T	1 050	0.15	1.0	0.8	24.0-27.0	—	Ti5.C-0.90	Sheets, rods, tubes
12X18H9	850	0.12	0.8	2.0	17.0-19.0	8.0-10.0	—	Ditto
10X23H18	1 050	0.10	1.0	2.0	22.0-25.0	17.0-20.0	—	Sheets, rods
12X25H16Г7AP	1 100	0.12	1.0	7.0	23.0-26.0	15.0-18.0	0.30-0.45 N; 0.010 B	Ditto
XH32T	1 100	0.05	0.7	0.7	19.0-22.0	30.0-34.0	0.25-0.60 Ti; 0.5 Al	Sheets, rods, tubes
XH45Ю	1 400	0.10	1.0	1.0	15.0-17.0	44.0-46.0	2.9-3.9 Al	Ditto
XH78T	1 150	0.12	0.8	0.7	19.0-22.0	Base (6.0% Fe)	0.15-0.35 Ti; 0.15 Al	Sheets, rods
15X25TЛ	1 050	0.1-0.2	0.5-1.2	0.5-0.8	28.0-27.0	—	0.40-0.80 Ti	Castings
30X24H12CЛ	1 050	0.4	0.5-1.5	0.3-0.8	22.0-26.0	11.0-13.0	—	Ditto
15X25H19C2Л	1 150	0.2	2.0-3.0	0.5-1.5	23.0-27.0	18.0-20.0	—	Ditto

Note. All are iron-base alloys except for Grade XH78T which is based on nickel (and contains up to 6.0% Fe

[1] Temperature of the beginning of intensive oxidation.

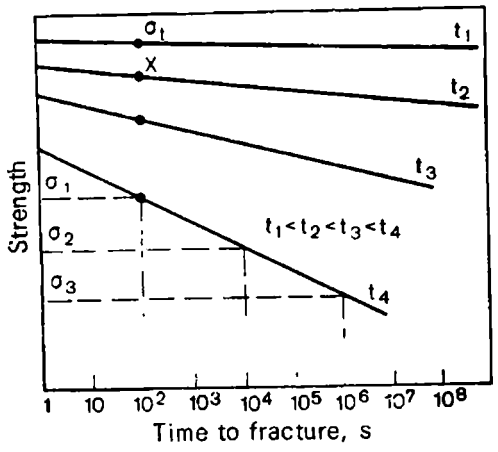

Fig. 18.4. Time-to-fracture *versus* strength diagram (N. S. Zhurkov)

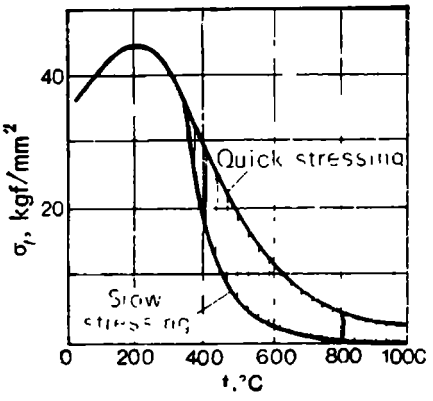

Fig. 18.5. Effect of test temperature on the ultimate strength of iron. In the shaded area, stresses cause creep

Figure 18.4 shows how the strength depends on the time of load application at various temperatures. Diagrams of this type are valid for many metals and alloys, so that the curves shown in the figure represent the tendency that is common to all metals. As seen from the diagram, the strength of a metal at a low temperature, say t_1^*, depends only slightly on the time of load application. For instance, if the stress is slightly lower than σ_t (denoted by X in the diagram), failure will occur only after a few tens of years ($> 10^9$ s). At higher temperatures, the dependence of strength on the time of load application becomes more pronounced (a greater slope of the curves). Finally, above a certain temperature, the strength decreases with increasing time of load application so quickly that it becomes senseless to indicate the allowable stress without giving the time of load application. Indeed, at temperature t_4 (Fig. 18.4), a stress σ_3 can cause failure in 10^6 s and a stress σ_1, in 10^2 s, i.e. 10 000 times more quickly.

It follows from the foregoing that the effect of time is negligible at low temperatures[1] and decisive, at elevated temperatures.

Therefore, taking into consideration the time factor, the strength of a metal should be characterized by what is called the *long-term strength*, which is the ultimate strength (ultimate resistance) at a given time of stressing or the stress that causes failure at a given

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* For some metals, such as steels, this is the room temperature.

[1] Naturally, this does not relate to quickly applied loads (impact loads) when the time to failure is only a fraction of a second and plastic deformation is delayed.

time of load application. Long-term strength is denoted by the Greek letter σ with a subscript indicating the time (hours) of stressing. For instance, σ_{100} is the stress that can cause failure in 100 hours.

At elevated temperatures, $\sigma_1 > \sigma_{10} > \sigma_{100} > \sigma_{300}$, etc., whereas at low temperatures they are practically equal, i.e. $\sigma_1 = \sigma_{10} = \sigma_{100} = \sigma_{1\,000} = \ldots = \sigma_t$.

Figure 18.5 shows the time-strength relationship for iron.

For iron and iron alloys, the strength at 200-300°C is higher than that at room temperature, but the ductility and toughness are lower (not shown in Fig. 18.5). The phenomenon is called *blue brittleness*[1].

In Fig. 18.5, the lower curve which begins at 350°C shows the strength of iron at an extremely low rate of stressing (let it be taken negligible in the further discussion) and the upper curve corresponds to the rates common in rupture tests of metal specimens (i.e. for short-term tests). Therefore, the temperature 350°C for iron is the temperature above which the metal becomes noticeably sensitive to test rate.

If the load can exceed the values determined by the upper curve, failure can occur at an increasing load.

If the stress is smaller than the value given by the lower curve, it will cause no failure. Finally, if the stresses are within the shaded region, failure will occur in a definite time interval, which is the shorter, the closer is the stress to the upper curve.

The stresses within the shaded area deform the metal in a definite time interval. This phenomenon, i.e. gradual deformation of a specimen under a constant stress is called *creep*.

Creep phenomena are examined by special instruments which automatically record what is called the *creep curve*, i.e. time variations of the deformation of a specimen under a constant stress. A typical creep curve is shown in Fig. 18.6.

A creep curve has a number of characteristic portions:

Portion *OA*—the curve of elastic and plastic deformations appearing at the moment of load application.

Portion *AB*; this is what is called transient portion; the metal is deformed with an unstable (decelerating) rate.

Portion *BC*—region of stable creep. The metal is deformed at a constant rate. The tangent of the curve characterizes the rate of creep.

Portion *CD* is the last stage of creep which occurs acceleratedly and is finished by failure at point *D*.

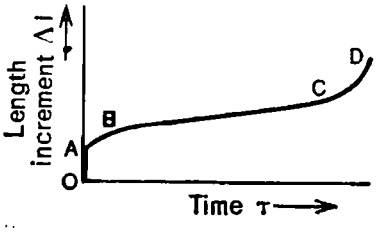

Fig. 18.6. Typical creep curve

[1] The temperature of appearance of blue brittleness corresponds to the blue temper colour of the metal surface. The phenomenon has no satisfactory explanation as yet.

Thus, it can be concluded that a stress above a definite limit, when applied at a temperature also above a definite limit, causes a metal to deform continuously under a constant load up to failure. Below the limiting value of stress and temperature, the phenomenon of creep is not observed[1].

The phenomena related to creep processes in metals can be described as follows.

A plastic deformation causes strengthening (work hardening) of a metal. The effect of work hardening is eliminated at a high temperature when the mobility of atoms is sufficiently high. Thus, two competing processes take place in creep of metals: work hardening due to plastic deformation and elimination of this effect, i.e. softening, under the action of a high temperature.

Below the temperature at which the process of softening can occur with a noticeable rate (350°C for iron), there is practically no creep. Thus, the temperature of softening determines the upper temperature limit above which a metal begins to creep.

If the stress at a given temperature (probably above the recrystallization point) is lower than the ultimate strength of the metal at the same temperature, it evidently will cause only elastic deformation. Since there is no plastic deformation, there is no work hardening, and therefore there can be neither softening nor creep.

Consequently, the phenomenon of creep can take place in the following instances: (a) at temperatures above the recrystallization point[2] and (b) at stresses above the elastic limit.

It then follows that the rate of creep should be higher in metals which can be softened more quickly through the recrystallization processes (which are determined by the strength of interatomic bonds) or at a lower strength in short-term tests.

In order to avoid creep completely, the recrystallization point of a metal should be raised above the working temperature or the elastic limit should be raised above the working stress at a given temperature.

It is not always possible to fulfil these two conditions at once, so that creep in real structures is often only retarded instead of being prevented fully. Since the rate of creep depends on the composition and structure of the metal, efforts are made to diminish it by proper alloying or by heat treatment. These measures can decrease the rate of softening at a given temperature (owing to the formation of stronger atomic bonds in the metal) and diminish the plastic deformation

[1] Strictly speaking, this is not so. Experimental studies show that creep can occur at any temperatures and stresses, but the process at low temperatures and stresses (below the definite limits) takes place at a very slow rate and can be neglected (see Fig. 18.4).

[2] More strictly, above the temperature at which softening can take place in work-hardened metal.

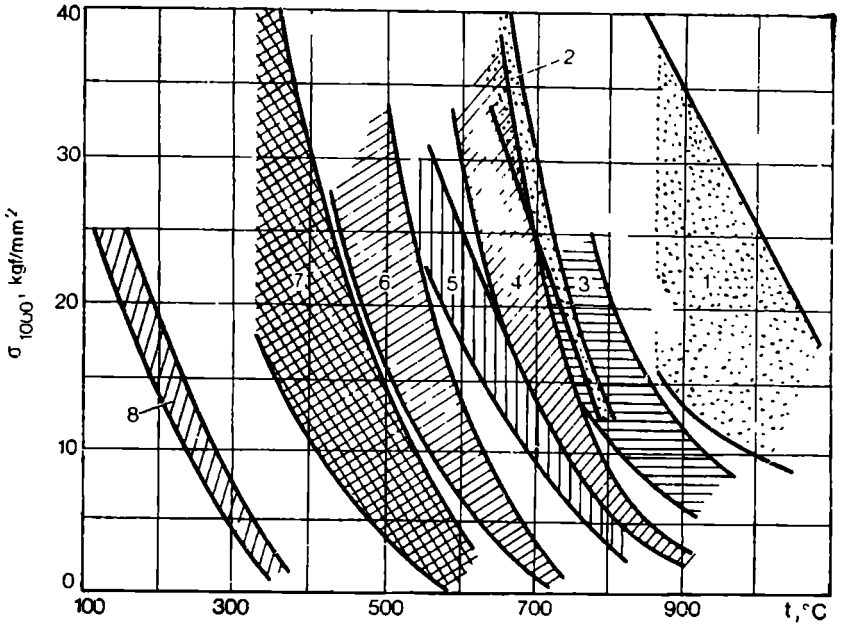

Fig. 18.7. Effect of temperature on long-term (1 000 h) strength of various metals
1 — molybdenum alloys; *2* — nickel alloys; *3* — cobalt alloys; *4* — Fe-Cr-Ni-Co alloys; *5* — austenitic steels; *6* — heat-resisting steels; *7* — titanium alloys; *8* — aluminium alloys

for a given stress, i.e. increase the strength of an alloy at a given temperature.

As noted earlier, a higher melting point of a metal has a correspondingly higher temperature of recrystallization. This is why high-melting metals are employed in structures of which a high heat-resistance is required. Since even the short-term strength drops noticeably on approaching the melting point, the highest working temperature (absolute) of metals should not exceed 0.7-0.8 of the melting point (K). In that connection, aluminium alloys can operate at the working temperatures not above 250°C (for aluminium, $T_{m.p.}$ = 657°C), iron-base alloys, up to 700°C ($T_{m.p.}$ = 1 530°C), and molybdenum-base alloys, up to 1 200-1 400°C ($T_{m.p.}$ = 2 600°C).

The heat-resisting properties of some alloys based on various metals are shown in Fig. 18.7. The highest heat resistance is exhibited by molybdenum-base alloys, which is due in the first place to the high melting point of molybdenum, and the lowest heat resistance, by alloys based on aluminium which has a low melting point.

The melting point of an alloy is not however directly indicative of the working temperature at which the alloy can be used. For some alloys this temperature is 0.7 to 0.8 of the melting point (K), whereas for others it is less than 0.5 of $T_{m.p.}$. For instance, copper alloys have turned out to be no more heat-resisting than aluminium alloys, though their melting points differ quite substantially

($T_{m.p.} \approx 600°C$ for aluminium alloys and $T_{m.p.} \approx 900°C$ for copper alloys).

The heat resistance of alloys in a particular group can be varied within definite limits determined by the scatter bands which depend on the alloying and structural state of a particular alloy (Fig. 18.7).

Thus, the heat-resisting properties of an alloy are decided in the first place by its base metal, then by the degree of alloying, and finally, by the prior heat treatment which has produced a particular structural state. As seen from Fig. 18.7, heat-resistance bands become narrower at higher temperatures; this means that the effect of alloying and heat treatment (structural state) diminishes with increasing temperature.

Considering the development of heat-resisting alloys from a historical standpoint, it might be concluded that every group of alloys has already exhausted its possibilities. Nevertheless, there are certain ways for further improvement of heat-resisting alloys.

1. The new industrial metallurgical processes produce metals of higher purity and, what is important, of higher density, which is achieved by the formation of an oriented crystallization front.
2. New processes of deforming have been or are being developed, so that certain alloys which were regarded as unsuitable for plastic working can now be deformed.
3. Some elements which earlier have been considered 'exotic' or too expensive are now used, naturally, to a limited scale, as alloying additions and even as alloy bases (tantalum, rhenium, hafnium, niobium, etc.).
4. New, principally novel ideas have been suggested for the manufacture of heat-resisting elements (composite materials, monocrystalline materials, etc.).
5. The metallurgical science has extended and deepened its knowledge of the nature of metallic materials, the mechanisms of strength and heat resistance; test methods are being perfected.

It should not be thought that the progress in technology can by itself increase the heat resistance. New processes of manufacture and heat treatment of alloys can ensure an increase in the heat resistance of alloys only in combination with changes in the alloy composition.

For instance, for the same content of the main alloying elements, a purer vacuum-refined metal may even have a lower heat resistance, but the greater ductility of the purer metal makes it possible to increase the content of a strengthening disperse phase and thus obtain a higher heat resistance. It may be supposed that this effect is due to a higher solubility of the strengthening phase in the purer metal and to the greater volume of disperse inclusions.

18.3. ESTIMATION OF HEAT-RESISTING PROPERTIES

The heat-resisting properties of a material cannot be characterized by a single parameter, since the requirements to heat-resisting materials are quite diverse.

For instance, a stationary gas turbine is intended for a few-year operation; naturally, the heat resistance of its materials should be such that the creep deformation does not exceed a specified limit, for instance 1 per cent in 10 years.

An aircraft gas turbine is in operation for an appreciably shorter time, 300 to 3 000 hours. The working stresses in that case can be substantially higher. An intercontinental missile is in flight only a few tens of minutes, whereas the first or second stage of a satellite launcher operates only a few seconds. In these cases, therefore, the material should have the 'long-term' strength of only a few minutes or seconds.

In modern metallurgy, the following characteristics of heat resistance are used.

The *creep limit* (σ_{pl}) is the stress that produces a given rate of deformation at given temperature. For instance, the creep limit can be characterized by the stress that causes a total deformation of 1 per cent in 300 hours (in portion *OAB*, see Fig. 18.6).

With parts operating for a long time (years), their creep limit should be characterized by a low deformation that appears when a load is applied for an appreciably long time. In such cases, only the deformation accumulating in a portion of a stable rate of creep (portion *BC* in Fig. 18.6) is taken into consideration. A tolerable strain limit (for instance, 1% in 10 000 h or 0.1% in 100 000 h, etc.) is also pre-assigned for that portion.

In the case considered, the stresses corresponding to the creep limit will evidently be substantially lower than, for instance, at 1-per cent deformation in 300 h. The creep limit is lower at a higher temperature and lower allowable deformation.

The *long-term strength* (σ_l) is the stress that causes failure at a given temperature in a given time interval.

If this time interval is taken as 100 hours, the stress that will cause failure in that time interval will be the long-term (100-h) strength. A stress causing failure in 300 h will evidently be lower than the former 100-h stress.

The heat resistance of materials can be characterized more fully by combined graphs, rather than by single characteristics (σ_{pl} or σ_l). Fig. 18.8 illustrates a combined graph for an alloy for making turbine blades. These graphs are plotted in logarithmic scales ($\log \sigma - \log \tau$) and characterize the heat-resisting properties at a given temperature and various duration of the tests.

The upper curve in the figure gives the stress that causes failure of specimens and the other curves show the relationship between stresses and strains for a given time interval.

For instance, a stress of 35 kgf/mm² causes failure in 1 000 h (i.e. $\sigma_{1\,000} = 35$ kgf/mm² at the given temperature), whereas a stress of 20 kgf/mm² will cause a deformation of only 0.1 per cent in the same time (i.e. $\sigma_{0.1/1\,000} = 20$ kgf/mm² at the same temperature). As may be seen, the time-stress relationship in logarithmic coordinates has the form of inclined straight lines. The lines have been obtained experimentally up to a test time of 1 000 h and prolonged further by extrapolation (dotted lines). The validity of such an extrapolation has not however been verified, so that reliable conclusions on the behaviour of a material at a higher temperature or longer time of performance can only be obtained by respective tests for the same time interval (which is not always possible practically).

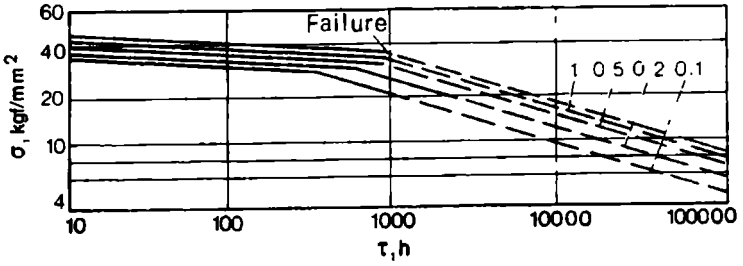

Fig. 18.8. Combined diagrams of the heat-resisting properties of Nimonic alloys (0.03% C, 19.7% Cr, 74.9% Ni, 2.6% Ti, and 0.9% Al) at a test temperature of 700°C. Numbers at curves — deformation, %

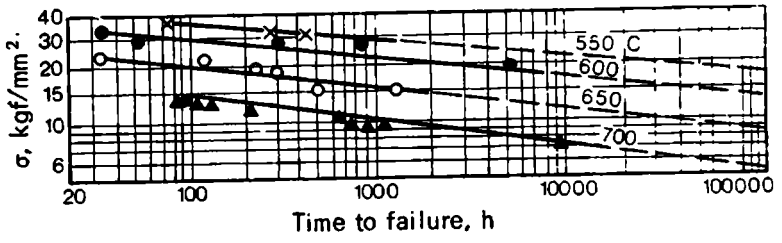

Fig. 18.9. Long-term strength of steel X14H14B2M at various temperatures

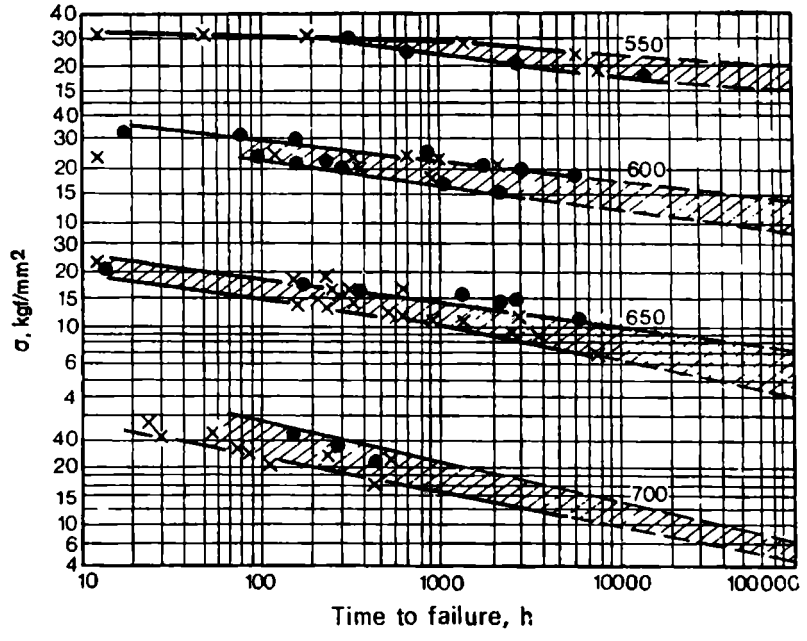

Fig. 18.10. Long-term strength bands of steel X18H9T

The combined graph as shown in Fig. 18.8 can sufficiently fully characterize the heat-resisting properties of an alloy at a given temperature (at 700°C in the case considered).

The heat resistance at different temperatures is most often estimated on a combined graph of long-term strength, in which each line gives the long-term strength at a particular temperature (Fig. 18.9).

As in Fig. 18.8, the lines in that figure characterize the properties of a steel from a particular melt. Various melts of the same steel grade may be different in composition according to the allowable variations in the content of elements, which naturally gives variations in the heat-resisting properties. This is why the heat resistance of a steel grade is characterized not by a line (in log σ — log τ coordinates), but by a band, as shown in Fig. 18.10).

18.4. EFFECT OF STRUCTURE AND COMPOSITION ON HEAT RESISTANCE

As noted earlier, the heat resistance is higher at a greater force of interatomic bonds and greater ultimate (short-term) strength at a given temperature.

It is natural in that connection that the heat resistance of alloys should be higher at a higher melting point.

It may also be concluded from the diagram in Fig. 18.7 that a higher melting point should give a higher heat resistance[1]. As has been noted earlier, the melting point determines the temperature of recrystallization, and the processes of recrystallization and softening determine in turn the rate of creep and heat resistance.

The temperatures of melting and recrystallization are functionally correlated by the equation:

$T_r = aT_{m.p.}$

where a is a coefficient depending on the composition and structure of an alloy. For very pure metals, $a \approx 0.2$, for metals of common purity, $a \approx 0.4$, and for concentrated solid solutions, $a = 0.7$-0.8.

It then follows that solid solutions, in the first place those with the elements that can raise the temperature of recrystallization, should be preferred as heat-resisting alloys.

Thus, solid-solution alloying increases the total level of strength of alloys at all values of temperature and, as a rule, increases the heat resistance (Fig. 18.11)[2].

This, however, does not exhaust the role of alloying. The solid solution of elements which can raise the temperature of recrystallization T_r should be highly concentrated and, what is most important, supersaturated to be capable of additional strengthening through precipitation hardening.

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[1] This conclusion is only valid at an appreciable difference of the melting points of two metals. With a slight difference, a metal having a lower melting point may turn out to have a higher heat resistance owing to some additional factors.

[2] Provided that the melting point has not been lowered appreciably.

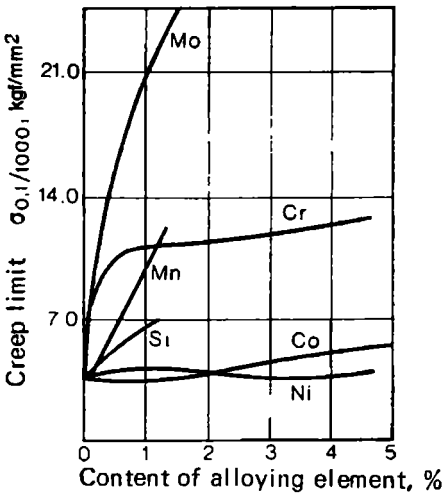

Fig. 18.11. Effect of dissolved elements on long-term strength of iron

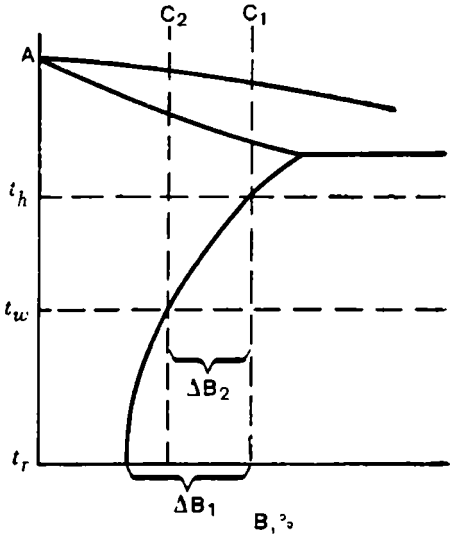

Fig. 18.12.

Let this be explained by the diagram in Fig. 18.12. Hardening of an alloy C_1 from temperature t_h produces a solid solution of supersaturation ΔB_1 at room temperature and ΔB_2 at the working temperature. Supersaturation will cause precipitation hardening whose effect may be quite different depending on the type of alloy and the extent of decomposition[1].

Naturally, the strengthening of an alloy by precipitation hardening increases the strength; on the other hand, 'overageing' of an alloy, i.e. softening due to coagulation of the excess phase, can lower the heat resistance.

This suggests the following conclusions:

(1) if an alloy is intended for short-term applications, it is preferable that the second phase in it be highly disperse; this can be achieved by common heat treatment, namely, hardening and tempering (ageing) at a temperature close to t_w, see Fig. 18.12. In the *A-B* system, the alloy C_1 is suitable for the purpose. In that case the rate of coagulation of the second phase (which produces the softening effect[2]) is of importance: a higher rate of this process implies a shorter service life of the alloy and a lower working temperature. A more complicated alloy, especially with a more complicated composition of the precipitated phase, can give a higher heat resistance.

(2) if an alloy is intended for long-term operation, of high importance becomes what is called the structural stability. The strength

[1] The strengthening effect is known to be high at the early stages of decomposition and then becomes lower owing to coagulation of precipitates.

[2] The softening effect is an inverse of the effect of red hardness in high-speed steels.

of alloys is known to decrease in the course of phase and structure changes, so that the coagulation process will have an adverse effect on the heat-resisting properties of the alloy considered.

Alloys which are not susceptible to precipitation hardening are more suitable for long-term operation. In the *A-B* system, it is the alloy of concentration C_2 (Fig. 18.12).

It is possible to take an alloy with a higher concentration of component *B* but which is in a stable structural state, i.e. in the state when coagulation of the second phase has finished in it. Experience shows, however, that the presence of a second coagulated phase has, as a rule, no effect on heat resistance. Therefore, excessive alloying[1] is ineffective. An exception to this is the application of casting alloys. In that case heavy alloying, even to the formation of a eutectic component, is quite admissible. The eutectic will form a brittle skeleton which will strengthen the matrix, as it were, and give a higher ultimate strength, but a lower ductility.

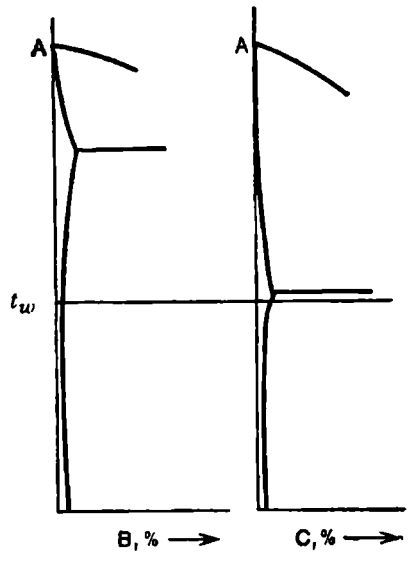

Fig. 18.13.

We have considered the alloying with elements possessing an appreciable solubility in the base metal. No strengthening effect due to the alloying of the solid solution and the processes of precipitation hardening will, however, be observed if the alloying elements used are poorly soluble in the base metal. In that case the melting point of the eutectic and precipitated phases becomes of exceptional importance. For instance, as shown in Fig. 18.13, the two components (*B* and *C*) are poorly soluble in base metal *A*, but an alloy with component *B* forms a eutectic whose melting point is well above the working temperature, whereas an alloy with component *C* forms a eutectic whose melting point is close to the working temperature. It may be then concluded that the presence of component *C* has an adverse effect on the heat resistance of an alloy and this component should be regarded as a harmful impurity.

This is why refining (by particular metallurgical techniques or by using a clean charge) of metal from harmful impurities which might form low-melting phases and eutectics is an important means for increasing the heat resistance of alloys. Examples of harmful impurities of this kind are low-melting metals, such as tin, lead, and anti-

[1] Above the concentration C_2 for alloys for long-term operation, and above C_1 for those for short-term operation.

mony, and also sulphur and some other elements. Certain elements can neutralize the harmful effect by combining with impurity elements and forming higher-melting compounds. Such, for instance, is the effect of cerium in nickel alloys.

If the base of a heat-resisting alloy has several allotropic forms, it is essential to obtain in the matrix the modification having a higher temperature of recrystallization. An alloy with a f.c.c. lattice (C12) is known to have a higher temperature of recrystallization than an alloy of a similar composition, but with a b.c.c. lattice (C8), i.e. an austenitic structure is more heat-resistant than a ferritic structure. This is probably associated with the higher density of the f.c.c. lattice. In that connection, alloys based on α-Ti (lattice number H12) are more heat-resistant than those based on β-Ti (C8).

Finally, heat resistance depends on grain size. Coarser grains give a higher heat resistance (A.M. Borzdyka), though at the expense of ductility.

18.5. CLASSIFICATION OF HEAT-RESISTING ALLOYS

It should be remembered that the mechanical properties of various alloys may vary differently with temperature. The designer should be able to select an alloy having the optimal combination of strength properties in a particular temperature range.

Figure 18.14 shows the short-term mechanical strength (ultimate strength) of various groups of alloys at different temperatures.

Below 300°C, plain carbon steels heat treated to a high strength have the highest ultimate strength (curve *1*). Creep phenomena are not probable at temperatures below 350-300°C, so that plain carbon steel can operate reliably at temperatures up to 300°C and it is of no necessity to employ special heat-resisting steels or alloys.

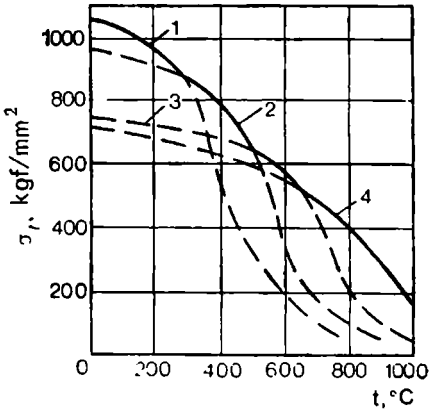

Fig. 18.14. Ultimate strength (short-term) of various alloys depending on test temperature (summarized schematically from various sources)

1 — Cr-Ni structural steel; *2* — ferritic scale-resisting steel; *3* — austenitic heat-resisting steel; *4* — — heat-resisting nickel alloy.

For the temperature range of 350-500°C, low-alloyed steels of pearlitic or ferritic class turn out to be optimal (curve *2*). At higher temperatures (500-650°C) the strength of these steels drops down abruptly and they become inferior to austenitic-class steels (curve *3*). At temperatures of 650-900°C, austenitic steels are excelled by high-alloyed cobalt and nickel alloys (curve *4*). At temperatures above 900°C, alloys of high-melting metals (molybdenum, chromium, etc.) are the best choice.

These temperature ranges are only approximate. At lower working stresses, some alloys can be used at temperatures above the temperature range specified for them; this is often favourable technologically or economically[1].

In the further discussion, we shall describe in more detail alloys for steam boilers (for working temperatures of 350-550°C and less frequently, 600-650°C), steam turbines and some related branches of engineering (for working temperatures of 500-650°C), gas turbines and missiles (for working temperatures above 650°C). Pearlitic and austenitic steels, nickel- and cobalt-base alloys and alloys of high-melting metals[2] will be discussed.

18.6. PEARLITIC AND MARTENSITIC HEAT-RESISTING STEELS

Let us consider the steels employed in steam power plant construction for the manufacture of steam pipelines, superheaters, fittings and other elements subjected to long-term mechanical actions at moderately high temperatures (up to 500-600°C). These are mostly

Table 18.2. Composition (%) of Heat-resisting Boiler Steels

Steel type (% Cr)	Steel Grade	C	Cr	Mo	Nb	V
			Pearlitic steels			
1	12MX	0.09-0.16	0.4-0.6	0.4-0.6	—	—
	12XMΦ	0.08-0.15	0.4-0.6	0.25-0.35	—	0.15-0.30
	12XM	0.09-0.16	0.8-1.1	0.4-0.6	—	—
	12X1MΦ	0.08-0.15	0.9-1.2	0.25-0.35	—	0.15-0.30
			Martensitic steels			
2	12X2MΦCP	0.08-0.15	1.6-1.9	0.5-0.7	—	0.20-0.35
	12X2MΦБ	0.08-0.12	2.1-2.6	0.5-0.7	—	0.20-0.35
5	X5BΦ	0.15	4.0-6.0	—	0.4-0.7	0.4-0.6
			Martensite-ferritic steels			
12	15X11MΦ	0.12-0.19	10-11.5	0.6-0.8	—	0.25-0.40
	1X12BHMΦ	0.12-0.18	11-13	0.5-0.7	0.7-1.1	0.15-0.30
	1X12B2MΦ	0.10-0.17	11-13	0.6-0.9	1.7-2.2	0.15-0.35

Note. In all these steels: < 0.04% S; < 0.04% P; 0.4-0.7% Mn; 0.17-0.37% Si (except for Grade 12X2MΦCP which contains 0.4-0.7% Si and 0.002-0.005% B); < 0.3% Ni (except for steels with 12% Cr which contain 0.4-0.8% Ni). Steel Grade 12X2MΦБ contains 0.5-0.8% Nb and Grade 1X12BHMΦ, 0.5-0.8% Ni.

[1] For instance, nickel-base alloys can sometimes be used at temperatures up to 1 000°C instead of more expensive heat-resisting alloys of high-melting metals.

[2] On high-melting metals see Ch. 22.

pearlitic-class steels and sometimes martensitic (bainitic) and ferritic steels. A typical feature of all these steels is that their matrix is α-solid solution and the excess phase is formed by carbides of various structure and origin.

Since steam power plant elements have to operate for an appreciable time (a few ten thousand hours) without replacement and should not deform appreciably during the operation, the principal characteristic of their metal is the creep limit at a deformation of 1 per cent in 10 000 hours or even in 100 000-200 000 hours.

The compositions of selected boiler steels are given in Table 18.2.

All the steels indicated contain less than 0.15-0.18% C, since they are mainly used for making pipes to be joined by butt welding, and a higher carbon content would impair the weldability.

In pearlitic-class steels, a slight addition of molybdenum increases the temperature of recrystallization of ferrite and thus increases the heat resistance. A similar but a weaker effect is produced by chromium (see Fig. 18.11).

Pearlitic-class steels are relatively low-alloyed steels and usually contain 0.5 to 1% Cr and 0.3 to 0.5% Mo at 0.12% C. An addition of vanadium refines the grain and increases the heat resistance. The steels have a pearlitic structure with M_3C carbide upon air cooling and martensite + bainite, upon oil quenching. The common heat treatment is oil quenching or normalizing followed by tempering (in both cases) at 720-750°C (Ac_1 = 760°C). Pearlitic-class steels are low in chromium and naturally cannot have a high heat resistance, i.e. cannot be employed at temperatures above 550-580°C.

A heavier alloying with chromium increases the heat resistance and makes a steel martensitic. Martensitic-class steels can be either air-cooled or oil-quenched. A hardened steel should be tempered at a temperature above the working value.

Owing to a higher chromium content, these steels have a higher scale resistance, and also a higher heat resistance [owing to the formation of special $M_{23}C_6$ carbides which coagulate more slowly than cementite (M_3C)].

An addition of tungsten, molybdenum or vanadium to a steel with 12% Cr can increase the heat resistance, but only to a definite limit, since at a higher content of these elements a steel becomes semi-ferritic and the $\alpha \rightleftarrows \gamma$ transformation in it will be incomplete[1], which can adversely affect the steel properties.

The principal heat-resisting properties of these steels are given in Tables 18.3 and 18.4.

Among these steels, the pearlitic low-alloy carbon steel (see Table 18.3) possesses the poorest heat-resisting properties. Alloying with 1% Cr and 0.5% Mo increases appreciably the heat resistance at 500°C. The martensitic-class steel (with 12% Cr) has a higher heat resistance than the pearlitic grade, but is inferior to the austenitic steel at temperatures above 600°C.

More detailed data on the heat-resisting properties of one of these steels (Grade 12ХМФ) are given in Fig. 18.15.

Though all these steels have a nearly equilibrium structure (ferrite + carbides) upon hardening and tempering, a long heating can however cause unwanted additional changes which impair the heat-resistance and ductility. These changes include the processes of spheroidization and graphitization of carbides (resulting in a lower heat resistance) and precipitation of excess phases on grain boundaries (resulting in *red shortness*). These phenomena can be avoided by an

[1] Recall that chromium, tungsten, molybdenum and vanadium are ferrite-forming elements which wedge out the γ-region.

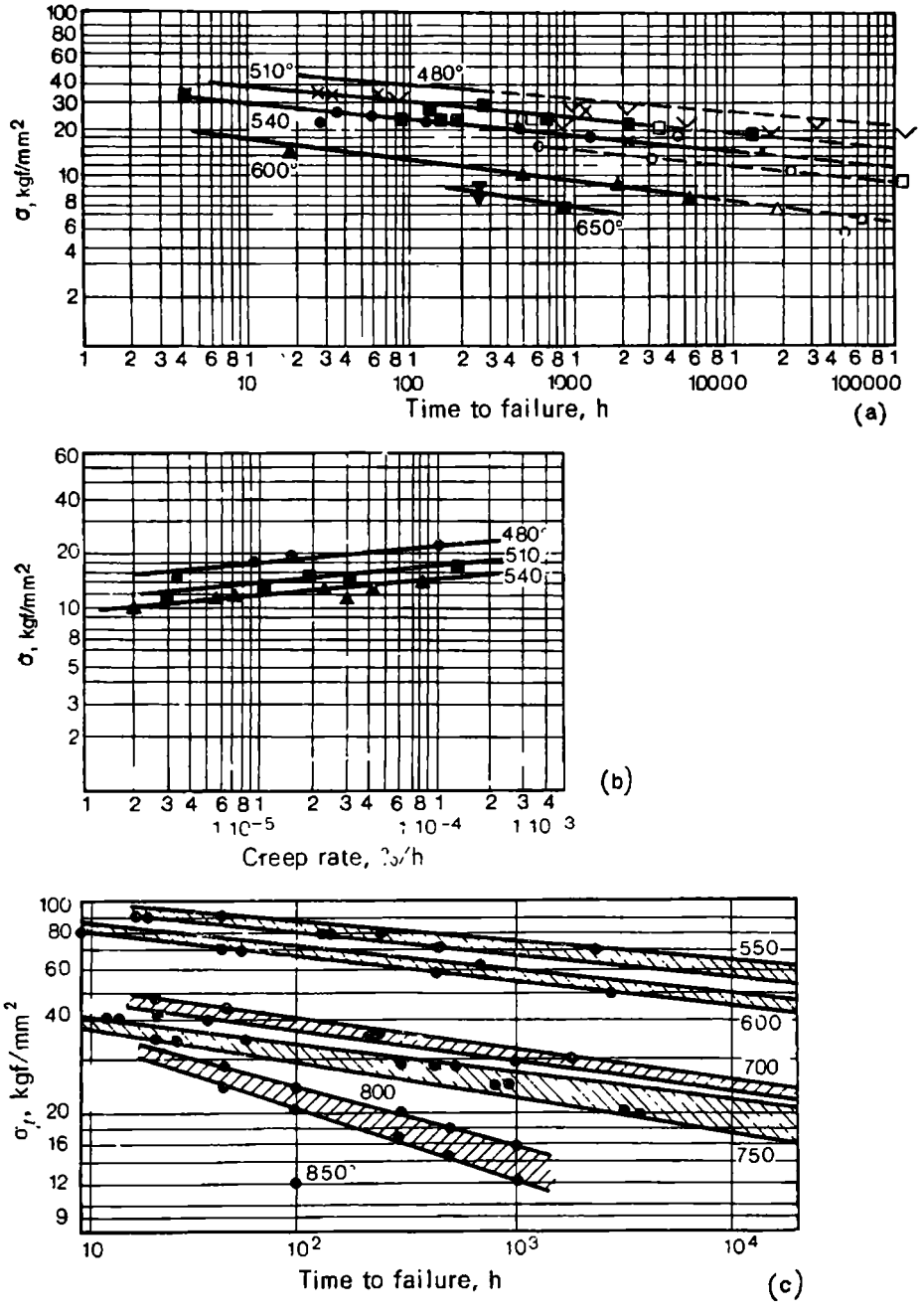

Fig. 18.15. Heat-resisting properties of steels 12ХМФ (*a*, *b*) (K.A. Lanskaya and ХН35ВТЮ (*c*) (M.V. Pridantsev)

appropriate heat treatment (also a heat treatment to restore the properties after a certain time of operation).

Apart from the more complex steel grades, simple chromium steels (with 12% Cr) of various carbon content are also employed for the purpose, mostly as stainless steels[1] but in some cases (for instance, in turbine blades), as heat-

[1] Stainless steels will be discussed in more detail in Ch. 19.

Table 18.3. Heat-resisting Properties of Pearlitic, Martensitic and Austenitic Boiler Steels

Content of elements	Long-term strength $\sigma_{l/100\,000}$, kgf/mm², at temperature, °C						
	400	450	500	550	600	650	700
Pearlitic							
1% Cr; 0.5% Mo	16	10	5	—	—	—	—
	—	—	15	7	—	—	—
Martensitic							
12% Cr; 1% Mo, V, W	—	—	20	15	6	—	—
Austenitic							
16% Cr; 13%Ni; 0.5% Nb	—	—	—	16	11	8	4

Table 18.4. Heat-resisting Properties (kgf/mm²) of Pearlitic and Martensitic Boiler Steels

Steel Grade	520°C		550°C		600°C	
	σ_l, 10 000 h	σ_{pl} 1%, 10 000 h	σ_l 1%, 10 000 h	σ_{pl} 1%, 10 000 h	σ_l 1%, 10 000 h	σ_{pl} 1%, 10 000 h
12MX	18	12	—	—	—	—
12XMΦ (12MXΦ)	19	10	—	—	—	—
15XM	18-20	—	—	—	—	—
12XHMΦ (12XMΦ)	—	—	13	9	8.5	—
12X2MΦCP	—	—	11.5	7.5	9.5	7
15X12BMΦ (ЭИ802)	—	—	15-19	—	14-16	—
12X12B2MΦ (ЭИ756)	—	—	17	—	15	—
1X13	22	9.5	—	—	—	—

resisting; their properties are given in Table 18.4. As may be seen, simple 12%-Cr steels are less heat-resisting than the more complex steels of the same type.

Figure 18.16 shows the temperature dependence for the long-term strength (100 000 h) of various heat-resisting steels.

The steels given in Table 18.3 are mainly boiler steels and are principally employed in pipes. If a high weldability is not very essential, high-chromium high-silicon steels (*silchromes*) can be used for the purpose.

The compositions of silchrome steels are given in Table 18.5.

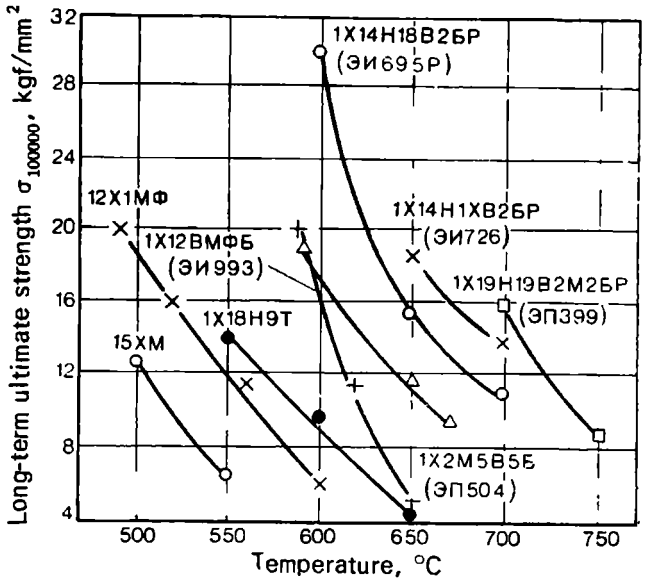

Fig. 18.16. Effect of temperature on long-term strength (100 000 h) of boiler steels (K.A. Lanskaya)

Silchrome steels are used for making exhaust valves of tractor, motor car and motocycle engines. The high chromium and silicon contents make them

Table 18.5. Compositions (%) of Silchrome Steels (GOST 5632—72)

Steel Grade	C	Cr	Si	Mo	Ni
X6C	<0.15	5.0-6.5	1.5-2.0	—	<0.6
X9C2	0.35-0.50	8.0-9.0	2.0-3.0	—	<0.6
X6CM	<0.15	5.0-6.5	1.5-2.0	0.45-0.60	<0.6
X7MC	<0.15	6.5-8.0	1.5-2.0	0.45-0.60	<0.6
X10C2M	0.35-0.45	9.0-10.5	1.9-2.6	0.70-0.90	<0.6
X13H7C2	0.25-0.37	11.0-14.5	2.0-3.0	—	6.0-7.5

Note. The steels may contain up to 0.7% Mn and 0.03% S and P.

resisting to oxidation. Intensive oxidation of these steels begins at different temperatures:

Steel Grade . . .	X6C	X6CM, X7CM	X9C2	X10C2M	X13H7C2
t,°C	750	800	850	900	1 000

The heat resistance of silchrome steels increases with heavier alloying (the silchrome grades in Table 18.5 are given in the order of increasing heat resistance).

The short-term strength of selected silchrome steels is given in Table 18.6.

Silchrome steels are heat-treated by hardening and tempering. Since chromium and silicon raise appreciably the critical points, the recommended heat-

Table 18.6. Ultimate Strength of Selected Silchrome Steels

Steel Grade	σ_t, kgf/mm², at various temperatures, °C						
	20	500	600	700	800	900	1 000
X10C2M	95	60	40	16	6	3	2
X13H7C2	120	80	40	30	20	15	6

treatment temperatures are higher than for common structural steels: 1 000-1 050°C for hardening and 750-780°C for tempering.

18.7. AUSTENITIC HEAT-RESISTING STEELS

Austenitic heat-resisting steels are used for making motor valves, gas-turbine blades and some 'hot' members of jet engines, mainly for operation at 600-700°C.

All austenitic heat-resisting steels are high in chromium and nickel and may also contain some other alloying elements.

Austenitic heat-resisting steels have high values of heat resistance, scale resistance, ductility, weldability, and linear expansion. Nevertheless they are inferior to pearlitic and martensitic steels in the processing properties, i.e. are less suitable for plastic working and machining, have a higher brittleness in welds; a coarse-grained structure formed owing to overheating cannot be corrected by heat treatment, since there is no structural recrystallization in them. These steels are often embrittled in the temperature range from 550 to 600°C owing to the precipitation of various phases on grain boundaries.

Austenitic steels can be classified into two groups:

(1) those which cannot be strengthened by heat treatment, i.e. not susceptible to precipitation hardening (they may be conditionally called homogeneous steels, though really they do contain second phases, but in quantities which cannot cause an appreciable age-hardening effect);

(2) those which can be and are strengthened by heat treatment (hardening + tempering). The strengthening effect is due to the precipitation of carbide, carbonitride or intermetallic phases. Their capability of ageing is due to the presence of certain elements (except for chromium and nickel) in quantities exceeding the solubility limit.

Chromium and nickel are the principal alloying elements in these steels. The former determines the scale resistance and the latter, the stability of austenite. With an insufficiently high nickel content in a steel, partial formation of α-phase is possible, which impairs the heat resistance.

The compositions of the principal grades of austenitic heat-resisting steels are given in Table 18.7. The steels of the first ('homogeneous') group can be employed as either heat-resisting or stainless and will be discussed in more detail in the next chapter; here we shall confine ourselves to the discussion of their scale resistance and heat resistance (see Table 18.8).

Table 18.7. Compositions, %, of Heat-resisting Austenitic Steels (GOST 5632—72)

Steel Grade	C	Cr	Ni	Other alloying elements
	Homogeneous steels			
1Х14Н16Б (ЭИ694)	0.07-0.12	13-15	14-17	0.9-1.3 Nb
1Х14Н18В2Б	0.07-0.12	13-15	18-20	2.0-2.7 W 0.9-1.3 Nb
Х18Н10Т	0.12	17-19	9-11	0.5-0.7 Ti
Х18Н12Т	0.12	17-19	11-13	0.5-0.7 Ti
0Х18Н12Б	0.08	17-19	11-13	8 C-1.2 Nb
1Х23Н18	0.20	22-25	17-20	—
Х25Н16Г7АР (ЭИ835)	0.12	23-25	15-18	0.3-0.45 N
Х25Н20С2 (ЭИ283)	0.20	24-27	18-21	—
	Precipitation-hardening steels			
4Х12Н8Г8МФБ (ЭИ481)	0.34-0.40	11.0-13.5	7-9	1.1-1.4 Mo 0.25-0.45 Nb 1.2-1.5 V
Х12Н20В3Т (ЭИ695)	0.10	10-12.5	18-21	2.6-3.2 W
4Х14Н14В2М (ЭИ69)	0.4-0.5	11-13	13-15	2.0-2.7 W 0.2-0.4 Mo
0Х14Н28В3Т3ЮР (ЭИ786)	0.08	13-15	26-29	2.8-3.5 W 2.4-3.2 Ti 0.5-1.2 Al

Note. The steels may contain 1-2% Mn (except for Grades 4Х12Н8Г8МФБ and Х25Н16Г7АР which contain respectively 7.5-9.5 and 5-7% Mn); up to 0.08% Si (except for Grade Х25Н20С2 which has 2-3% Si); up to 0.02% S and 0.035% P. The steels with the letter P in the designation contain roughly 0.002% B.

The typical heat treatment of these steels is heating to 1 050-1 100°C followed by water quenching or air cooling, after which the steel is stabilized (tempered) at 750°C, the procedure resulting in the coagulation of small amounts of the second phase (mainly of chromium carbides of the type $M_{23}C_6$) present in the steel and stabilization of the structure.

A long exposure to the working temperature (500-700°C), embrittles the steel owing to the precipitation of excess phases on grain boundaries and to what is called *sigmatization*, i.e. precipitation of σ-phase, an intermetallide of the FeCr type. These transformations are rather sluggish.

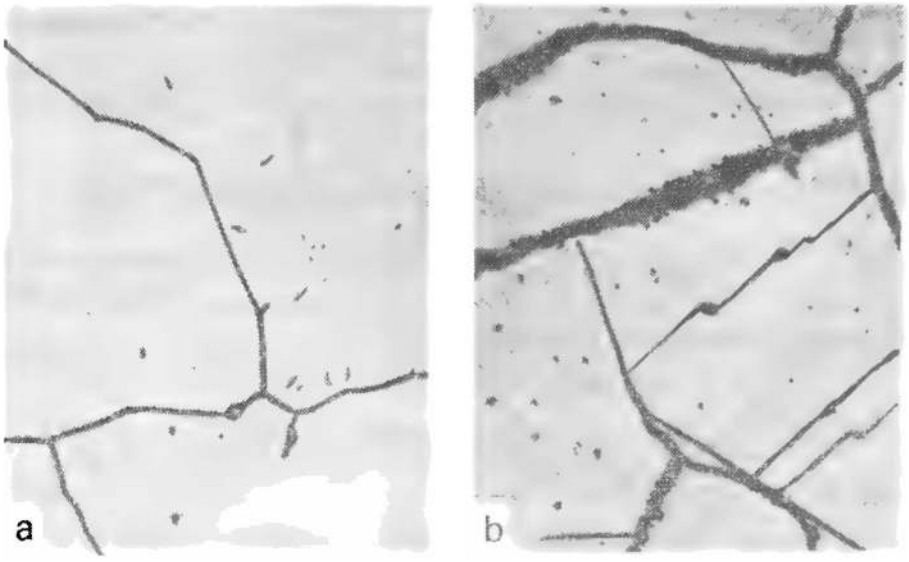

Fig. 18.17. Microstructures of heat-resisting austenitic steel. ×500
(*a*) as hardened; (*b*) as tempered at 650°C

The steels of the second group, unlike those of the first, are unstable and prone to strengthening due to the decomposition of the solid solution (which lowers the toughness).

The heat treatment of these steels consists in water quenching from 1 050-1 100°C and tempering (ageing) at 600-750°C. The ageing—tempering increases the hardness owing to the precipitation-hardening effect; excess phases precipitate in ageing mainly on grain boundaries (See Fig. 18.17).

Naturally, the role of this heat treatment is to raise the heat resistance. The austenitic steels of the second group exhibit a higher heat resistance than

Table 18.8. Properties of Selected Austenitic (Homogeneous) Steels

Steel Grade	Scale resistance[1], °C	Short-term strength σ_t, kgf/mm²			Long-term strength, kgf/mm²			
					σ_{100}		σ_{1000}	
		600°C	700°C	800°C	600°C	700°C	600°C	700°C
1X18H10T	800	35	30	25	25	12	20	10
X18H12Б	800	38	33	28	28	15	22	12
1X14H18B2БP	750	45	42	—	35	24	28	17
1X14H18B2Б	750	45	38	—	35	24	30	18

[1] Temperature of the beginning of intensive oxidation.

Table 18.9. Heat-resisting Properties of Selected Precipitation-hardening Austenitic Steels

Steel Grade	Short-term strength, kgf/mm²			Long-term strength, kgt/mm²	
	600°C	700°C	800°C	600°C	700°C
4Х14Н14В2М (ЭИ69)	50	35	23	23	13
4Х12Н8Г8МФБ (ЭИ481)	60	50	—	45	30
Х12Н20Т3Р (ЭИ696)	85	70	40	55	40

the homogeneous austenitic steels, which may be explained by greater dispersion of the second phases, though this circumstance is of advantage only in short-term operation: with a long time of operation ($\tau > 100$ h), the strengthening excess phase can coagulate and diminish the heat resistance below that of the homogeneous alloys. This may be clearly seen from the data given in Tables 18.8 and 18.9.

Apart from the steels described, which have a diverse application, there are austenitic heat-resisting steels for more special applications (elements of furnaces, retorts, covering sheets, etc.). The compositions and scale resistance of some special heat and scale resisting steels have been given in Table 18.1.

18.8. HEAT-RESISTING NICKEL AND COBALT ALLOYS

Turbine blades are the most critical members in modern gas turbines and jet engines. The power of a jet engine depends to a large extent on the maximum temperature of the heat carrier (gas), at which the blades can operate for a long time. The blades of modern jet engines are heated to 700-900°C in operation and there is a tendency for increasing this temperature in the future.

Turbine blades are made of austenitic steels or alloys based on nickel or cobalt.

The preferable application have nickel alloys which as a rule contain chromium (15-20%) and other quite numerous though minor additions (aluminium, titanium, tungsten, molybdenum, vanadium, etc.).

Like austenitic steels, nickel-base alloys can be divided into homogeneous (called *nichromes* and *inconels*) and age-hardening (*nimonic*-type alloys).

The former, i.e. nichromes, are alloys of nickel and chromium or of nickel, chromium and iron with the minimized content of carbon and other elements which might form second phases. The structure of these alloys is a solid solution of these elements in nickel (f.c.c. lattice). A homogeneous solid solution possesses neither a high strength nor a high heat resistance. Alloys of this type are usually employed in members operating at slight or no loads, i.e. they are used as scale-resisting, rather than as heat-resisting materials; these

alloys have found application in electric resistance heaters which will be discussed in Ch. 24 where the compositions and selected properties of nichromes are indicated.

Age-hardening nickel-base alloys (nimonics) are actually used as heat-resisting alloys. Their appearance was due to the fast progress in jet aviation which demanded heat-resisting alloys for turbine blades, since the heat-resisting alloys (mainly austenitic steels) known to that time were not as heat-resisting as required.

Nimonic of the principal, 'classic' composition is a quarternary Ni-Cr-Ti-Al alloy (approximately 20% Cr, 1% Al, 2% Ti and nickel the balance). Hardening from 1050-1 150°C forms γ-solid solution with f.c.c. lattice (a = 3.57 Å).

When being heated, the hardened (supersaturated) solid solution passes through several stages of decomposition.

Initially, aluminium and titanium atoms in the solid solution are redistributed and cause local enrichment with these impurities. The process can be observed not only at low temperatures, but even during quenching[1].

At the next stage, a second phase appears, as it were, in places where the concentration of aluminium and titanium atoms has increased locally. At a definite stage of ageing, it is possible to detect radiographically two phases having the same crystal lattice (C12) but with slightly differing lattice parameters (3.58 and 3.60 Å). It has been adopted that the phase depleted of aluminium and titanium be called the γ-phase and that enriched with these elements (precipitated), the γ'-phase.

The former process, i.e. the redistribution of aluminium and titanium in the solid solution lattice, is observed during quenching and in tempering at 500-600°C, whereas the γ'-phase appears at temperatures of 600-850°C and its composition and particle size depend on the temperature and time of tempering (ageing). For instance, upon ageing for a few hours at 700°C, the volume of the γ'-phase may be 20 per cent of the alloy volume (or even more) and the size of its particles of an order of 200-400 Å. Because of the close similarity of their lattices, γ- and γ'-phase retain the coherent bond up to quite high temperatures of tempering. At a still higher temperature of ageing, γ'-phase can change into γ-phase (Ni_3Ti) which is stable at that temperature. These changes are reflected in the microstructure and properties of the alloy (see Fig. 18.18).

The high heat resistance of nimonic alloys is due to their high strength and low rate of softening. In the case considered, the high strength of an aged nimonic alloy is associated with the formation of a large quantity (up to 20% and in some modern high-heat resisting alloys, up to 40%) of the second phase which is coherent with the

[1] Suppression of this process by very fast quenching is undesirable.

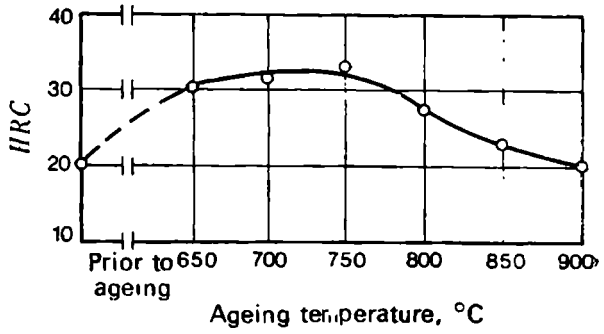

Fig. 18.18. Effect of ageing temperature on the hardness of nimonic alloys

solid solution of the matrix. This coherent bond, in turn, causes refinement of γ-solid solution blocks to a size of 1 500-2 000 Å. The low rate of softening is, in turn, due to the low diffusion mobility of aluminium and titanium atoms at high temperatures, owing to strong interatomic bonds in the lattices of γ- and γ′-phase.

At the temperatures 700-800°C, the rate of particle growth of the second phase is low, but becomes appreciable at 850-900°C (see Fig. 18.19), which determines the temperature and time limits of application of these alloys.

The heat treatment of nimonic alloys to bring them to the state of the highest heat resistance consists in air hardening from 1 100-1 200°C and tempering (ageing) at 700-750°C for 10-16 hours. The maximum heat resistance is obtained with a homogeneous coarse-grain structure and homogeneous uniformly distributed disperse formations of γ′-phase.

Inequigranularity (i.e. the presence of both large and fine grains in the structure), preferable precipitation of phases on the grain boundaries, and retention of the work-hardened state (for instance, upon machining) result in a lower heat resistance.

The compositions of the most popular grades of age-hardening nickel-base alloys are given in Table 18.10.

The heat-resisting properties of alloy type XH77TIO (0.2-% deformation in different time) are shown in Fig. 18.20.

The principal heat-resisting properties of selected nickel-base alloys are also given in Table 18.11 and Fig. 18.21.

The 'oldest' alloy in this group, type XH77TIOP (also called Nimonic-80) has the lowest heat resistance (see Table 18.11). This alloy can be improved, in the first place, by small additions of boron and cerium (Grades XH77TIO and XH77TIOP, see also Fig. 18.21), which results in the 'cleaning' of grain boundaries. The main function of these additions is to combine harmful impurities into high-melting compounds.

A further increase in heat resistance is achieved by introducing elements which can strengthen the solid solution, such as cobalt, molybdenum or tungsten (Nimonic-90 and Nimonic-100 alloys).

The alloys given in Table 18.10 are the principal ones for the 'hot' elements of gas turbines (blades, discs, etc.).

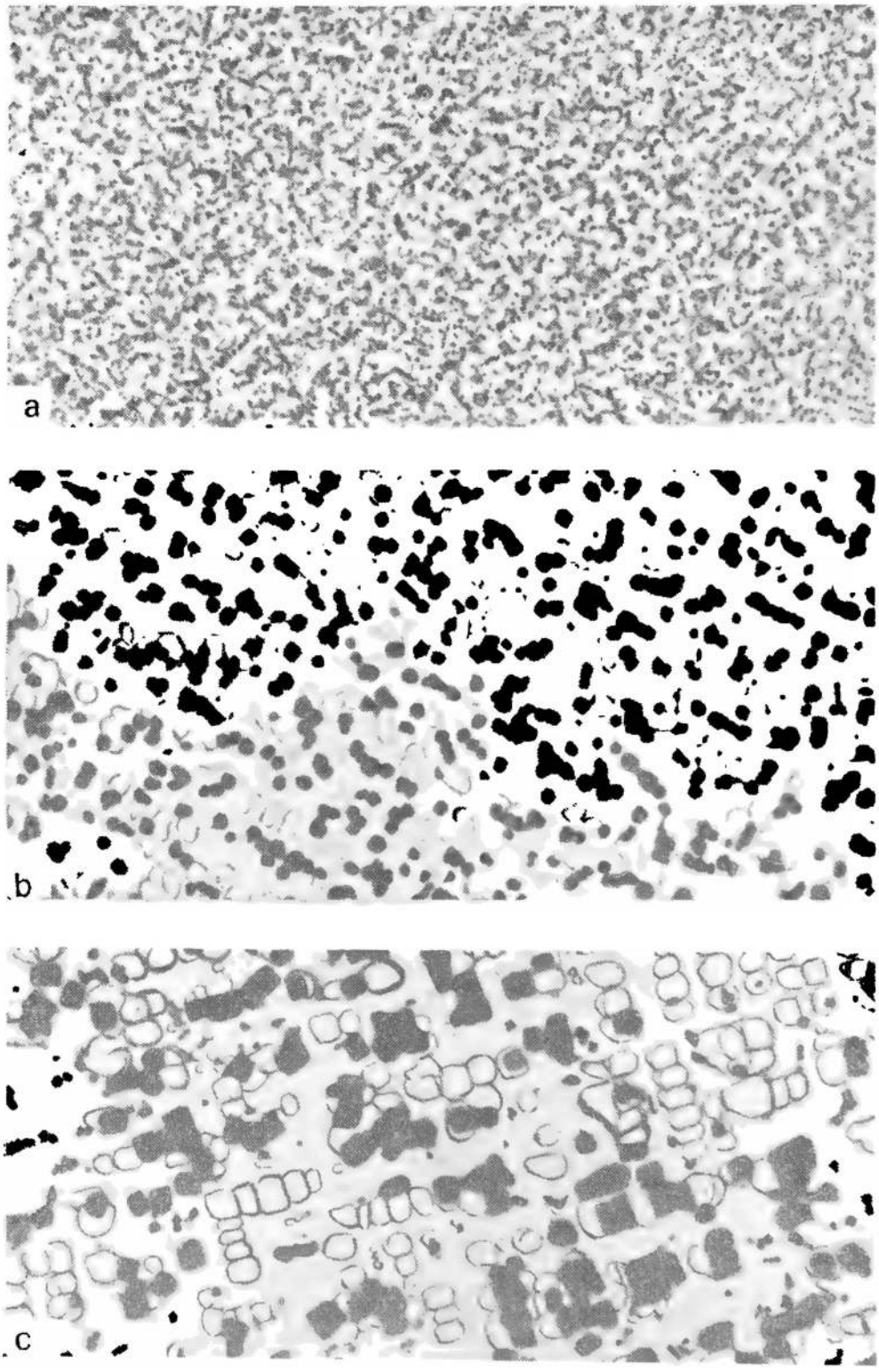

Fig. 18.19. Coagulation of Ni_3 (Ti, Al) particles in Nimonic alloy upon hardening and ageing at 850°C. ×15 000
(*a*) after 10 h; (*b*) after 100 h; (*c*) after 1 000 h

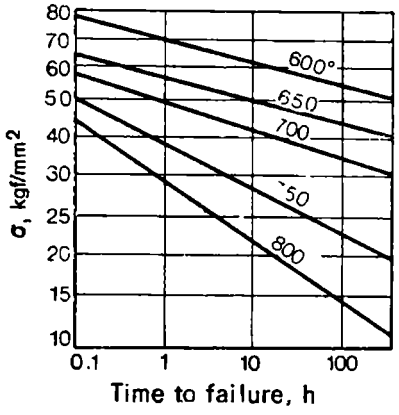

Fig. 18.20. Heat-resisting properties of Nimonic alloy (type XH77TЮP)

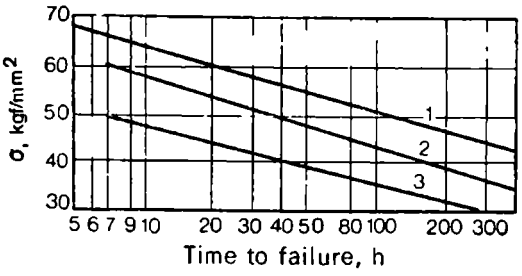

Fig. 18.21. Long-term strength of various nickel alloys at 700°C:

1 — XH70BMTЮ; *2* — XH77TЮP; *3* — XH77TЮ

Along with age-hardening nickel alloys, iron-nickel and cobalt alloys also find some application[1].

The compositions of some of these alloys are given in Table 18.12.

Table 18.10. Compositions of Age-hardening Heat-resisting Nickel Alloys (Nimonic), % (GOST 5632—72)

Alloy Grade	Cr	Ti	Al	Fe	C	Other elements
XH77TЮ (ЭИ437А)	19-22	2.3-2.7	0.55-0.95	4.0	0.06	⩽0.01 Ce
XH77TЮP (ЭИ437Б)	19-22	2.3-2.7	0.55-0.95	4.0	0.06	⩽0.01 Ce
XH70BMTЮ (ЭИ617)	13-16	1.8-2.3	1.7-2.3	5.0	0.12	5-7 W, 2-4 Mo, 0.1-0.5 V, ⩽0.02 B, ⩽0.02 Ce
Nimonic-90	18-21	2.0-2.8	0.8-1.2	1.0	0.10	15-21 Co
Nimonic-100	10-12	1-2	4-6	2.0	0.3	18-22 Co, 4.5-5.5 Mo

In their heat-resisting properties, iron-nickel and cobalt alloys are roughly equivalent to nickel-base (Nimonic) alloys. The iron-nickel alloys are however low-ductile and liable to cracking and other defects; cobalt-base alloys, on the other hand, are very expensive and not much superior over the best grades of nickel-base alloys as regards their heat resistance.

[1] They are close in their nature to nimonic alloys in which half of the nickel has been replaced by iron.

Table 18.11. Heat-resisting Properties of Selected Nickel Alloys

Alloy Grade	Short-term strength σ_t, kgf/mm²			Long-term strength, kgf/mm²					
				σ_{100}			$\sigma_{1\,000}$		
	600°C	700°C	800°C	600°C	700°C	800°C	600°C	700°C	800°C
ХН77ТЮ	88	68	55	58	36	14	—	28	10
ХН77ТЮР	95	85	56	68	42	20	—	35	12
ЭИ617	99	90	75	—	50	29	—	38	—
Nimonic-90	100	80	63	—	43	21	—	34	14
Nimonic-100	115	105	75	—	50	29	—	42	20

The upper temperature limit of application of nickel-base alloys is 950-1 000°C and other-base alloys should be employed at higher temperatures. Some data on the progress in the development of heat-resisting alloys are given in Table 18.13 (according to G. V. Estulin and S. B. Maslenkov).

Table 18.12. Compositions of Iron-nickel and Cobalt Heat-resisting Alloys, %

Alloy Grade	C	Cr	Ni	Mo	Al	W	Ti
Iron-nickel (iron-base) alloys							
ХН35ВТ (ЭИ612)	0.12	14-16	34-38	—	—	2.8-3.5	1.1-1.5
ХН35ВТЮ (ЭИ787)	0.08	14-16	33-37	—	0.7-1.4	2.8-3.5	2.4-3.2
Cobalt alloys (< 2% Fe)							
ЭИ416	0.35-0.45	18-21	18-22	3.5-5.8	—	3.8-5.8	—
Vitallium (ЛКУ)	0.20-0.35	25-30	1.5-3.5	4.5-6.5	—	—	—

Table 18.13. Development of Heat-resisting Alloys

Year	$\sigma = 35$kgf/mm² (for discs)		$\sigma = 20$ kgf/mm² (for blades)		$\sigma = 20$ kgf/mm² (for blades)	
	alloy Grade	working temperature, °C	alloy Grade	working temperature, °C	alloy Grade	working temperature, °C
	Deformable alloys				*Casting alloys*	
1946	0ХН3М	510	ЭИ69	650	—	—
1947	ЭИ415	590	ЭИ388	710	ЖС3	850
1948	—	—	—	—	—	—
1949	ЭИ395	650	ЭИ437	750	—	—
1950	ЭИ434	650	—	—	—	—
1951	ЭИ481	660	—	—	—	—
1952	ЭИ481Б	660	ХН77ТЮ	780	—	—
1953	ХН77	730	ХН77ТЮР	790	—	—
1954	—	—	ЭИ617	850	АНВ	900
1955	—	—	—	—	—	—
1956	—	—	ЭИ826	880	ЖС6	970
1958	—	—	ЭИ867	920	—	—
1960	ЭИ698	750	ЭИ929	920	—	—
1962	—	—	ЭП109	940	—	—
1963	ЭИ766	780	ЭП220	950	—	—
1966	—	—	—	—	ЖС6К (НК)	990

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Chapter 19

CORROSION-RESISTING (STAINLESS) STEELS AND ALLOYS

Corrosion is the deterioration of the metal surface under the action of a chemically aggressive medium. Pure iron and low-alloy steels are not corrosion-resisting in the atmospheric air, water and many other media, since the oxide film that forms on the surface is insufficiently dense and cannot protect the metal from the chemical action of the medium. Certain elements increase the corrosion resistance of steel and thus make it possible to obtain steels (or alloys) which do not practically corrode in a particular medium.

The corrosion resistance of steel increases not gradually but jumpwise upon addition of such elements. Without going into the details of the phenomena associated with corrosion and corrosion failure, it may be only noted that a steel alloyed with 12 or more per cent chromium becomes corrosion-resisting in atmospheric air and many industrial corrosive media. Steels (alloys) with less than 12% Cr virtually corrode as easily as iron, whereas alloys with more than 12-14% Cr behave much like noble metals: they possess a positive corrosion potential (Fig. 19.1) and are not oxidized in air, water and many acids and alkalis.

19.1. CHROMIUM STAINLESS STEELS

There are three types of chromium stainless steels: with 13, 17 and 27% Cr; steels with 12% Cr may have a different carbon content (from 0.1 to 0.4%) depending on their application.

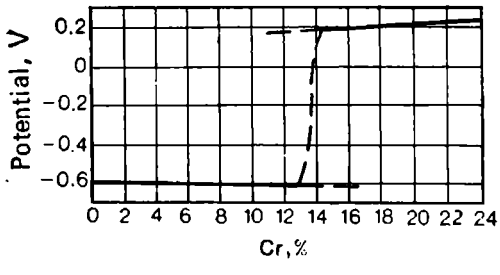

Fig. 19.1. Corrosion potential of Fe-Cr alloys

Steels with 17-18 and 25-28% Cr are sometimes alloyed with small additions of titanium and nickel. Both these elements are introduced for grain refinement and nickel in addition improves the mechanical properties.

The compositions of commercial chromium stainless steels are given in Table 19.1.

Table 19.1. Compositions of Chromium Stainless Steels, % (GOST 5632—72)

Class	Steel type (% Cr)	Steel Grade	C	Cr	Ti	Mn	Si
F	13	0X13	<0.08	11-13	—	⩽0.6	⩽0.6
M-F		1X13	0.09-0.15	12-14	—	⩽0.8	⩽0.8
M		2X13	0.16-0.25	12-14	—	⩽0.8	⩽0.8
M		3X13	0.26-0.35	12-14	—	⩽0.8	⩽0.8
M		4X13	0.36-0.45	12-14	—	⩽0.8	⩽0.8
F		X14	⩽0.15	13-15	—	⩽0.6	⩽0.6
F	17	12X17	⩽0.12	16-18	—	⩽0.8	⩽0.8
F		08X17T	⩽0.08	16-18	5C-0.8	⩽0.8	⩽0.8
M		14X17H2 *	0.11-0.17	16-18	—	⩽0.8	⩽0.8
F	25-28	15X25T	⩽0.15	24-27	5C-0.9	⩽0.8	⩽1.0
F		15X28	⩽0.15	27-30	—	⩽0.8	⩽1.0

Note. In all these steels: S < 0.025% and P < 0.030%. The content of titanium may be from at least five times that of carbon to 0.8-0.9%. M and F are respectively martensitic and ferritic class of steel.

* Contains 1.5-2.5% Ni.

Chromium stainless steels can be classified by their equilibrium structure with reference to the diagram of the ternary Fe-C-Cr system (Fig. 19.2). The rectangles in the figure determine the position of a particular steel grade in the system.

As may be seen, chromium steels with 12-14% Cr can belong to different structural classes depending on their carbon content, as is clear from Table 19.1. Steel 0X13 can be either purely ferritic (with the carbon content <0.09% and chromium content >13%) or semi-ferritic (at the average specified values of chromium and carbon). In the former case, the $\gamma \rightleftarrows \alpha$ transformation is complete and in the latter, only partial. A steel of the same grade but with the minimum content of chromium (12%) and the maximum content of carbon (0.15%) will undergo the complete $\gamma \rightarrow \alpha$ transformation and harden to martensite by air cooling from the γ-region.

Thus, the structure of this grade of steel can vary at small variations in its composition (within the limits specified for the grade) from ferritic to martensitic and its properties are rather unstable. The same may be said of steel Grades 1X13* and X14**.

* This grade can be either semi-ferritic or martensitic depending on the actual carbon and chromium content.

** This grade is usually ferritic, but can be semi-ferritic at the upper limit of carbon.

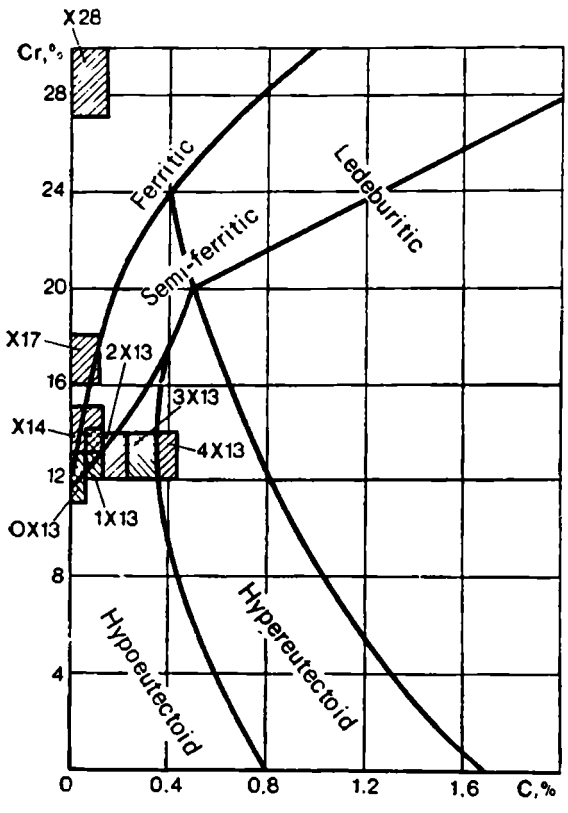

Fig. 19.2. Fe-C-Cr system and location of commercial stainless chromium steels in it

Steel Grades 2X13, 3X13 and 4X13 are martensitic-class steels and Grades X17 and X25-X28 are ferritic (Fig. 19.3).

In view of the foregoing, the structures of these steels upon hardening (or air cooling) from a high temperature (900-1 100°C) may be as follows: Grades 0X13 and 1X13 —ferrite and martensite (in various proportions; the structure of recrystallized ferrite usually prevails in steel 0X13, while Grade 1X13 contains little ferrite); Grades 2X13, 3X13, and 4X13—martensite; Grades 12X17, 15X25T, and 15X28—ferrite.

The suitability of a steel for heat treatment is determined by the extent of the $\gamma \rightleftarrows \alpha$ transformation in it (Fig. 19.4). A steel with 0.01% C and 13% Cr cannot be strengthened by hardening, since the $\gamma \rightleftarrows \alpha$ transformation does not take place in it; a steel with 0.35% C can be strengthened substantially by hardening from a temperature above 800°C (for this steel, Ac_1 = 800°C) due to the formation of martensite; steels with intermediate values of carbon content can be strengthened less appreciably by hardening, because to an incomplete $\alpha \rightleftarrows \gamma$ transformation and also since their martensite contains less carbon. Thus, the hardening temperature of steel Grade X13 should be varied depending on its carbon content (increased at a higher carbon content) in order to dissolve carbides as fully as possible and obtain a high hardness.

The typical conditions of heat treatment for chromium stainless steels and the values of mechanical properties obtained are given in Table 19.2.

The steels of the type X13 are the most popular and the least expensive among stainless steels; they are employed in domestic appliances and in industry (for making blades of hydraulic and steam turbines). They have a fair weldability. Steels with a low carbon content (1X13, 2X13) are quite ductile and can be easily stamped; Grades 3X13 and 4X13 have a high hardness and elevated strength and are used in parts where elevated values of strength and wear resistance and a high corrosion resistance are essential[1].

The group of steels with 17% Cr has a higher corrosion resistance than the former group. In view of their high content in chromium, steels type X17 can also be employed as scale-resisting at the working temperatures up to 900°C.

With an addition of nickel and an increased content of carbon the steels with 17% Cr undergo $\gamma \rightleftarrows \alpha$ transformation. Though the transformation is not complete, it produces a noticeable strengthening effect. In the group of steels with 17% Cr, Grade X17H2 is a high-strength steel (Table 19.2) and is employed

[1] Various tools, including surgical tools, ball bearings, springs and other parts for operation in active corrosive media.

Table 19.2. Conditions of Heat Treatment and Mechanical Properties of Chromium Stainless Steels

Steel Grade	Temperature, °C		Mechanical properties					
	of hardening	of tempering	*HRC*	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %	ψ, %	a_n kgf/cm²
12X13	1 000	700	—	60	40	20	60	90
2X13	1 050	700	—	85	65	10	50	60
3X13	1 050	250	40	160	130	—	—	—
4X13	1 050	200	50	—	—	—	—	—
12X17	1 050	750	—	45	30	15-25	40-50	2-5
08X17T, 14X17H2	1 050	300	—	110	90	10	35	5
15X25T, 15X28	1 050	750	—	45	30	20	45	—

in cases where an elevated strength is needed in addition to the corrosion resistance typical of this group.

The steels with 25-28% Cr are used for making furnace elements (muffles, thermocouple sheaths, retorts) for operation at the temperatures up to 1 050-1 150°C.

A serious drawback of these ferritic steels is that the coarse-grained structure appearing on overheating (for instance in welding) cannot be eliminated by heat treatment, since these steels undergo no phase transformations. A coarse-grained structure may also make the steel excessively brittle (the ductile-to-brittle transition point is raised and passes into the positive-temperature region). Grain coarsening in these steels can be suppressed somewhat by the additions of titanium and nitrogen (and also of vanadium) owing to the formation of titanium (vanadium) carbides which improve the mechanical properties.

The embrittling effect can also be observed in these steels even when their structure is fine-grained; in that case it is due to ordering processes (which can occur even on a short holding at 450-550°C) or to the precipitation of carbides on the grain boundaries (usually at higher temperatures, of an order of 600-700°C). In steels of the type X17 and especially in X28, a brittle σ-phase may form during a long holding near 700°C.

Advances in the steelmaking industry have made it possible to manufacture high-chromium steels (with 17% Cr or more) having a carbon content less than 0.005 per cent. These steels do not suffer from the drawbacks mentioned above, i.e. are not embrittled and can there-

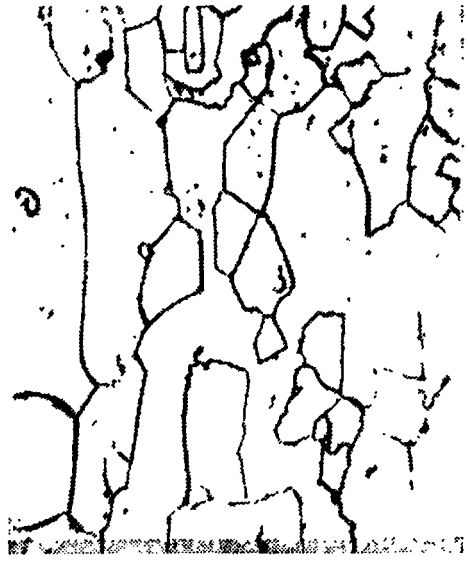

Fig. 19.3. Typical structure of ferritic stainless steel (X25T). ×400

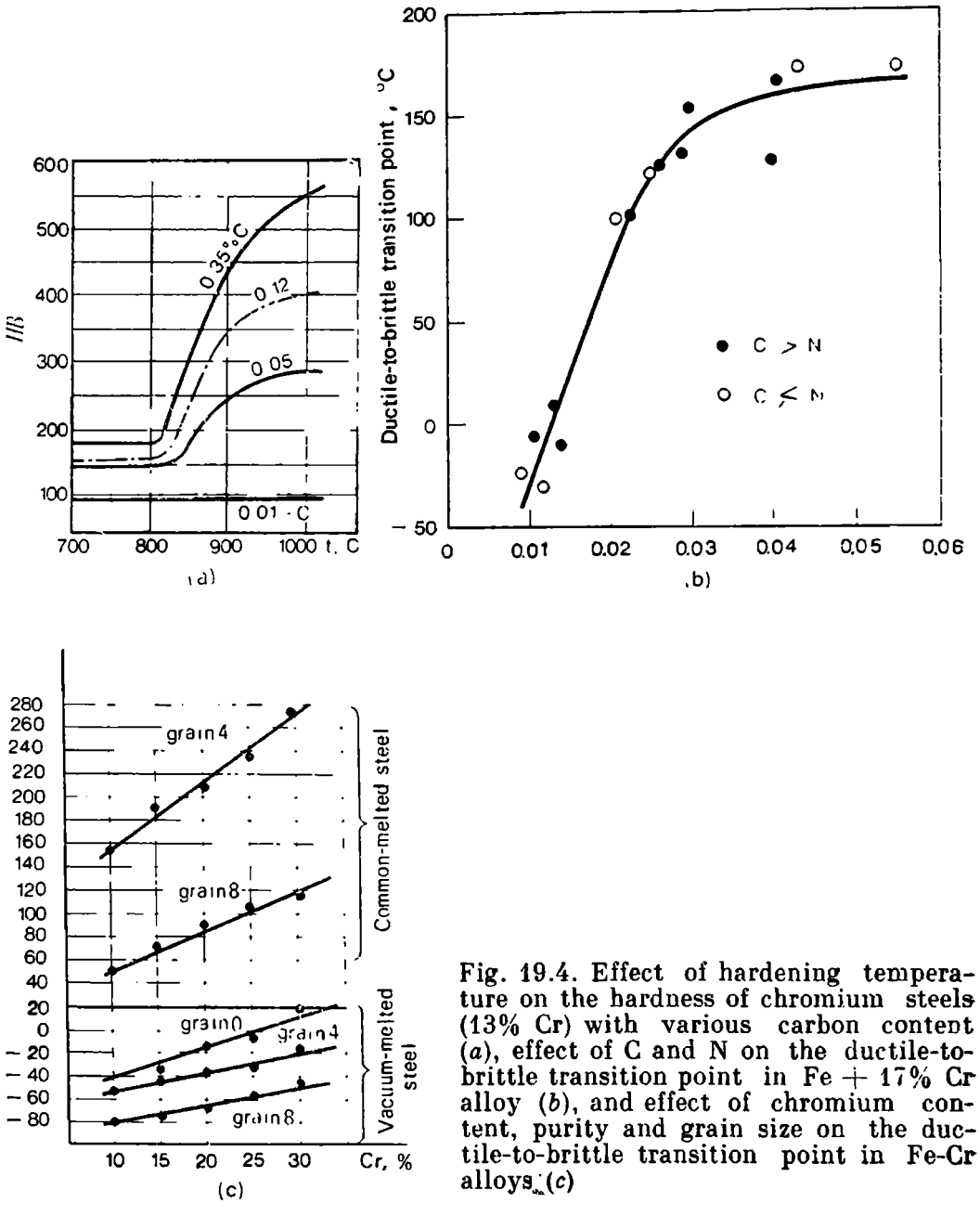

Fig. 19.4. Effect of hardening temperature on the hardness of chromium steels (13% Cr) with various carbon content (*a*), effect of C and N on the ductile-to-brittle transition point in Fe + 17% Cr alloy (*b*), and effect of chromium content, purity and grain size on the ductile-to-brittle transition point in Fe-Cr alloys (*c*)

fore be used in welded structures. These ferritic stainless steels are called *superferrites*.

Recent studies have shown that the ductile-to-brittle transition point can be lowered by diminishing the sum C + N (according to other data, the sum C + N + O), which must be not more than 0.02 or 0.03 per cent, respectively. The summing is quite possible, since these elements form interstitial solid solutions in α-iron, have quantitatively almost the same effect and have close values of the atomic weight (12, 14 and 16).

As can be seen from Fig. 19.4*b*, the sum C + N should be not more than 0.02 per cent in order to obtain a high impact toughness at room temperature.

As has been given earlier, welding causes grain coarsening in the weld-affected zone, most often to the grain size index of 0 or 1. Since stainless steels are used most often in welded structures, it is essential to ensure a proper toughness in the metal near the weld (the weld proper will always be quite tough if welding has been done with austenitic electrodes).

The general dependence of the ductile-to-brittle transition point on the principal factors—steel purity, grain size, and content of chromium, is shown in Fig. 19.4*c* from which it follows that (a) the ductile-to-brittle transition point is appreciably lower in steels clean from interstitial impurities; (b) the ductile-to-brittle transition point increases with a higher content of chromium or with grain coarsening.

Assuming that a proper weldability (absence of brittleness in a welded joint) is ensured at the grain size index of 0 by the position of the ductile-to-brittle transition point below room temperature, it may be taken that high-purity chromium alloys (superferrites, C + N + O <0.03%) can be welded at the chromium content up to 25 per cent.

19.2. CHROME-NICKEL STAINLESS STEELS

With an ample addition of nickel, 18%-Cr steel becomes austenitic in the whole temperature range, which improves its mechanical properties, makes it less susceptible to grain coarsening, eliminates cold brittleness, and increases corrosion resistance.

Stainless steels with 18% Cr and 10% Ni have found a very wide application in mechanical engineering, manufacture of consumer goods, and also in architecture and sculpture.

The formation of phases in Cr-Ni stainless steels can be examined by reference to the Fe-Cr-Ni system.

Figure 19.5 shows a horizontal section at 650°C through the Fe-Cr-Ni constitutional diagram (solid lines). The single-phase regions γ and α are separated from each other by the two-phase region $\gamma + \alpha$. At the chromium content more than 20 per cent there appears σ-phase (FeCr compound). The position of the two-phase $\gamma + \alpha$ region depends on temperature. With the temperature decreasing below 650°C, the $\gamma + \alpha$ region is shifted to the right and its rightmost position at 20°C is shown by the dotted lines terminating at points *c* and *g*. As the temperature rises, the region is shifted to the left and its leftmost position at 1 100°C is shown by the dotted lines terminating at points *a* and *d*.

It then follows that all alloys below the line *abc* should undergo full $\gamma \rightleftarrows \alpha$ recrystallization and have the structure of ferrite at room temperature. The lines *abc* and *defg* confine the region of semi-ferritic (or semi-austenitic) alloys under-

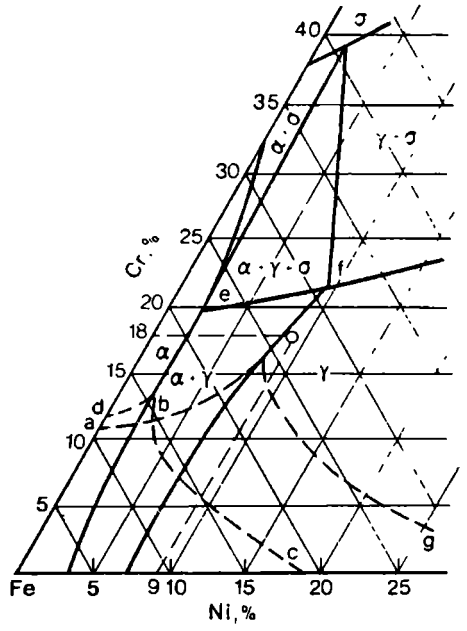

Fig. 19.5. Iron-rich corner of Fe-Cr-Ni system. Solid lines show isothermal section at 650°C

going partial $\gamma \rightleftarrows \alpha$ transformation. Alloys to the left of line *de* are ferritic (we have discussed them in the previous section); all alloys to the right of line *fg* are austenitic and will be discussed below.

An alloy with 18% Cr and 9% Ni is shown by a circle in the figure. It may be easily seen that for an alloy with 18% Cr to have an austenitic structure, its nickel content should be not less than 9 per cent; at a lower content of nickel the alloy becomes two-phase in the whole temperature range (i.e. at room temperature as well). The same results are obtained by increasing the content of chromium above 18 per cent (at 9% Ni). At a chromium content less than 14-15 per cent, α-phase appears in the structure; at temperatures below 650°C the formation of α-phase occurs by the martensitic mechanism[1].

Apart from the main austenitic γ-phase, Cr-Ni stainless steels can also contain α-phase in the following modifications: (a) α-phase formed by precipitation from the liquid or from austenite at high temperatures (above 600-700°C) and (b) α'-phase which forms from austenite at low temperatures (below 600°C) by the martensitic mechanism.

The austenitic state of alloys with 18% Cr and 8-15% Ni can be either stable or unstable depending on variations in their composition. In the latter case, cooling of an alloy to a low temperature (below 0°C) can result in the formation of martensite (α'); this transformation can also be induced by plastic deformation (α''). Plastic deformation at a low temperature can in some cases cause the formation of what is called hexagonal ε-martensite (at intermediate state) which then transforms into common α-martensite.

Austenite with 18% Cr and 8-10% Ni is practically unstable and can be transformed into martensite by cooling to a sub-zero temperature or by plastic deformation at room temperature. In alloys with 18% Cr and 10-12% Ni, the formation of martensite can only be induced by plastic deformation at temperatures below 0°C. Alloys with 18% Cr and more than 14% Ni are however very stable in the austenitic state; α-phase can be formed in them neither by cooling nor by low-temperature deformation. A typical structure of stainless steel (austenite) is shown in Fig. 19.6.

Commercial Cr-Ni steels naturally are not pure Fe-Cr-Ni alloys, but contain certain impurities. These impurities can dissolve in the main phases (γ and α) and thus affect the equilibrium conditions and the kinetics of $\gamma \rightleftarrows \alpha$ transformation. If they form new phases, such as carbides, nitrides or intermetallides, they can affect substantially the properties of the steel, though their effect on the $\gamma \rightleftarrows \alpha$ transformation is less substantial.

The elements dissolved in γ- and α-phase can be divided into two groups: those promoting the $\gamma \rightarrow \alpha$ transformation (ferrite-forming elements) and those inhibiting this transformation (austenite-forming elements).

[1] At higher temperatures, α-phase usually forms by diffusion.

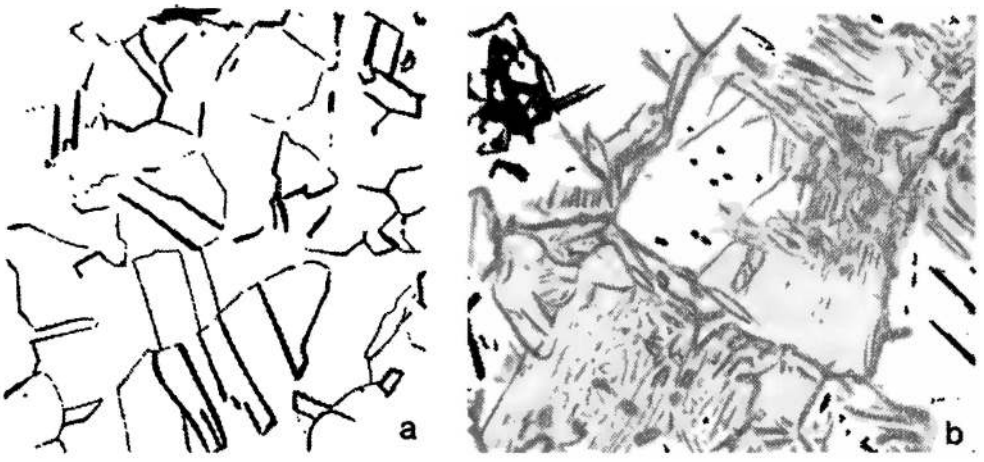

Fig. 19.6. Typical microstructure of stainless steel
(*a*) austenitic class (austenite). ×200; (*b*) intermediate class (austenite + martensite). ×500

Among the austenite-forming elements, i.e. those acting similar to nickel, are carbon, nitrogen and manganese; the ferrite-forming elements, whose effect is similar to an increase in the content of chromium, include molybdenum, tungsten, titanium, niobium, tantalum, and silicon. With Cr-Ni steels of a complex composition containing carbon, nitrogen, manganese, silicon, titanium and other elements, it is quite difficult to decide which structural group they belong to; the Fe-Cr-Ni ternary diagram (see Fig. 19.5) is useless in that case.

The problem can be solved by using a schematic diagram showing the structural state of an alloy at room temperature depending on its contents in ferrite- and austenite-forming elements (Fig. 19.7).

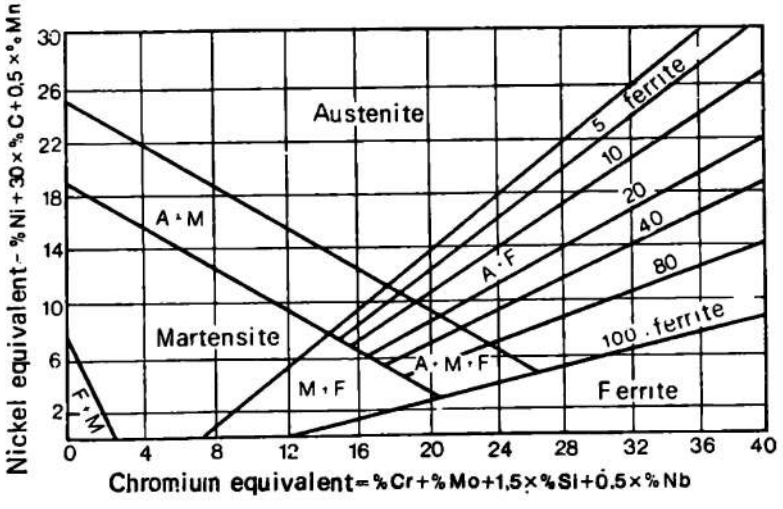

Fig. 19.7. Structural diagram of stainless steels

Table 19.3. Compositions of Cr-Ni

Nos.	Steel Grade	Class	Type	C
1	12Х18Н8 (ЭЯ1)	Austenitic	18-9	0.12
2	17Х18Н9 (ЭЯ2)			0.13-0.21
3	12Х18Н9Т (ЭЯ1Т)			0.12
4	04Х18Н10 (ЭИ842)		18-10	0.04
5	08Х18Н10 (ЭЯ0)			0.08
6	12Х18Н10Е (ЭП47)			0.12
7	08Х18Н10Т (ЭИ914)			0.08
8	12Х18Н10Т (ЭЯ1Т)			0.12
9	06Х18Н11 (ЭИ684)		18-12	0.06
10	08Х18Н12Т			0.08
11	12Х18Н12Т			0.12
12	08Х18Н12Б (ЭИ402)			0.08
13	10Х14Г14Н4Т (ЭИ711)		Cr-Ni-Mn	0.10
14	12Х17Г9АН4 (ЭИ878)			0.12
15	15Х17АГ14 (ЭП213)			0.15
16	10Х17Н13М2Т (ЭИ448)		Cr-Ni-Mo	0.10
17	10Х17Н13М3Т (ЭИ432)			0.10
18	09Х16Н15М3Б (ЭИ847)			0.09
19	06Х23Н28М3Д3Т (ЭИ943)		Cr-Ni-Mo-Cu	0.06
20	09Х15Н8Ю (ЭИ904)	Austenite-martensitic	—	0.09
21	09Х17Н7Ю (ЭИ973)			0.09
22	08Х22Н6Т (ЭП53)	Austenite-ferritic	21-5	0.08
23	12Х22Н5Т (ЭИ811)			0.09-0.14
24	08Х21Н6М2Т (ЭП54)			0.08
25	08Х18Г8Н2Т (КО3)		Cr-Ni-Mn	0.08

Stainless Steels, % (GOST 5632—72)

Mn	Cr	Ni	Ti	Mo	Nb	Other elements
1-2	17-19	8-10	—	—	—	—
1-2	17-19	8-10	—	—	—	—
1-2	17-19	8-9.5	5 C-0.08	—	—	—
1-2	17-19	9-11	—	—	—	—
1-2	17-19	9-11	—	—	—	—
1-2	17-19	9-11	—	—	—	0.18-0.35 Se
1-2	17-19	9-11	5 C-0.7	—	—	—
1-2	17-19	9-11	5 C-0.08	—	—	—
1-2	17-19	10-12	—	—	—	—
1-2	17-19	10-13	5 C-0.6	—	—	—
1-2	17-19	10-13	5 C-0.07	—	—	—
1-2	17-19	10-13	—	—	8 C-1.2	—
13-15	13-15	2.8-4.5	(C-0.02) 5-0.6	—	—	—
8-10.5	16-18	3.5-4.5	—	—	—	0.15-0.25 N
13.5-15.5	16-18	0.6	—	—	—	0.25-0.37 N
1-2	16-18	12-14	5 C-0.7	2.0-3.0	—	—
1-2	16-18	12-14	5 C-0.7	3-4	—	—
0.8	15-17	14-16	—	2.5-3.0	0.6-0.9	—
0.8	22-25	26-29	0.5-0.9	2.5-3.0	—	2.5-3.5 Cu
0.8	14-16	8-10	—	—	—	0.7-1.3 Al
0.8	16-17.5	7.0-8.0	—	—	—	0.5-0.8 Al
0.8	21-23	5.3-6.3	5 C-0.65	—	—	—
0.8	20-22	4.8-5.8	0.25-0.5	—	—	—
0.8	20-22	5.5-6.5	0.2-0.4	1.8-2.5	—	—
7-9	17-19	1.8-2.5	0.2-0.5	—	—	—

The effect of each of the elements is expressed as the effect of chromium or of nickel with a certain correction factor. For instance, the effect of carbon (as of austenite-forming element) is 30 times that of nickel; the effect of niobium is one-half that of chromium.

According to the diagram in Fig. 19.7, an alloy with 0.1% C, 2% Mn, 18% Cr, 12% Ni, and 2% Mo is austenitic (its composition is equivalent to 16% nickel and 20% chromium). For a steel with 22% Cr and the same content of the other elements, the equivalent of chromium will rise up to 24 per cent, and therefore, the steel will contain roughly 5 per cent of ferrite. If the nickel equivalent is lowered to 8 per cent and that of chromium to 20 per cent, the alloy will consist of austenite and two ferritic phases: $\alpha - \alpha'$; the former phase has formed at a high temperature and the latter at a low temperature: i.e. the structural state of the alloy can be described as $\gamma + \alpha + \alpha'$ at a low temperature and as $\gamma + \alpha$ at a high temperature.

In view of what has been said on the structures in chrome-nickel steels, the latter can be divided into three classes as follows:

(a) *austenitic steels*, i.e. those containing stable austenite;

(b) *austenite-martensitic steels* (or *transition-class* steels); they form a certain quantity of martensite on cooling (Fig. 19.6*b*); this class also includes the steels which have no indications of $\gamma \rightarrow \alpha$ transformation on cooling to room temperature but whose austenite is nonetheless unstable since it transforms into martensite on subzero treatment or plastic deformation;

(c) *austenite-ferritic steels* whose structure is $\alpha - \gamma$; their austenite may be either stable or unstable.

The regions of existence of these classes of steel are shown in Fig. 19.7.

The compositions of commercial Cr-Ni stainless steels are given in Table 19.3. The table contains not only the principal Cr-Ni alloys, including those additionally alloyed, but also the steels in which nickel is fully or partially replaced by manganese and nitrogen (steels with all the nickel replaced cannot naturally be called Cr-Ni steels).

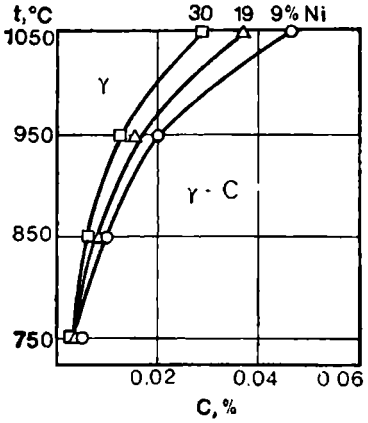

Fig. 19.8. Solubility of carbon (carbides) in austenite (after the author)

Since Cr-Ni stainless steels contain carbon, special carbides (preferably of the type $M_{23}C_6$) can form in them.

The content of these carbides naturally depends on the content in carbon. The solubility of carbon (carbides) in steel is very low (only 0.05%) in the temperature range from room temperature to approximately 700°C (Fig. 19.8), but increases rapidly at higher temperatures, so that 0.05% C can be dissolved at a temperature of 1 050°C; at temperatures of

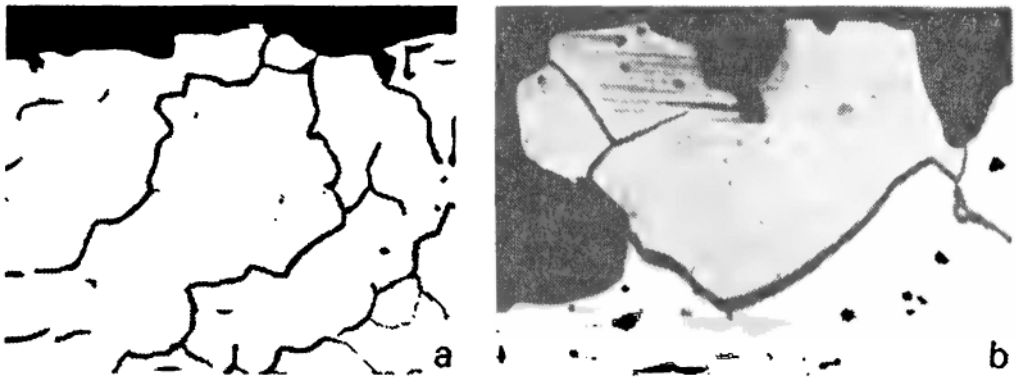

Fig. 19.9. Microstructure of austenitic stainless steel infected with intercrystalline corrosion
(*a*) ×300; (*b*) ×500

1150°C or higher all the carbides can be dissolved even if the steel contains 0.15% C (at a nickel content of 9%; nickel decreases the solubility of carbon in austenite at high temperatures). Naturally, with such a high difference in the solubility of carbides in austenite, a supersaturated solid solution can be formed by heating steel to a high temperature and quickly cooling (quenching) it, while repeated heating (at 500-700°C) will cause precipitation of the carbides.

Carbides precipitate on the grain boundaries, which under certain circumstances can cause embrittlement of the steel and the appearance of a special and very dangerous type of corrosion failure on the grain boundaries which is called *intercrystalline*, or *intergranular corrosion*.

A sheet of stainless steel infected by intercrystalline corrosion does not clink when being tapped and can break to pieces or powder under a slight load applied.

The effect of intercrystalline corrosion is associated with a reduction in the corrosion resistance of grain boundaries owing to the fact that almost all the carbon (which has enough time to diffuse from the bulk of grains) participates in the formation of the carbide phase ($M_{23}C_6$) on the grain boundaries, whereas the chromium entering into the composition of $M_{23}C_6$ carbide is supplied only from the boundary layers of grains, but not from the bulk of grains, since its rate of diffusion is too low. This results in that the solid solution on the grain boundaries contains less than 12% Cr, i.e. below the limit ensuring the corrosion resistance. It is exactly for that reason that corrosion cracking propagates into the depth of metal only along the grain boundaries which have been depleted of chromium[1] (Fig. 19.9).

As has been demonstrated by metallographic studies, intercrystalline corrosion occurs when the carbides that have precipitated on grain boundaries form

[1] This relates to corrosion in weakly oxidizing media. Intercrystalline corrosion in strongly oxidizing media develops through carbide inclusions since these are not stable in these media.

a continuous network. In cases where the precipitated carbides do not form a continuous network or where large carbide particles coagulate on grain boundaries, no intercrystalline corrosion takes place.

The effect of intercrystalline corrosion can only appear as a result of heating of a hardened austenitic steel within a certain temperature range (500-700°C), since this heating promotes precipitation of carbides on grain boundaries.

It should be clear that heating to 500-700°C can cause precipitation of carbides only in supersaturated austenite, i.e. in hardened austenitic steels (if their carbon content is more than 0.005%). The susceptibility of austenitic stainless steels to intercrystalline corrosion can be eliminated not only by lowering the carbon content, but also by adding certain stabilizing elements, such as titanium or niobium, which are strong carbide-formers. When added to a steel, titanium and niobium form carbides of *MC* type. These carbides (interstitial phases) are poorly soluble in austenite.

Titanium and niobium combine with carbon and thus prevent the formation of chromium carbides and appearance of intercrystalline corrosion. Naturally, titanium and niobium should be added in an ample quantity (sufficient to bind all the carbon).

The stabilizing elements (titanium and niobium) can only diminish intercrystalline corrosion and a more reliable method to prevent the development of intercrystalline corrosion is to lower the carbon content of steel.

A high resistance to intercrystalline corrosion in steels of this type can be obtained by stabilizing annealing (usually at a temperature near 850°C); in this method, carbides precipitate completely from the solution and coagulate, and chromium is distributed evenly over the volume of grains. Unfortunately, this method of heat treatment is effective not with all types of steel[1] and should be carried out only after welding, which in many cases is difficult to be done owing to large dimensions of welded structures.

The resistance of steels to intercrystalline corrosion can be characterized by typical C-shaped curves (Fig. 19.10). These curves determine the time of annealing in the dangerous temperature interval (called provoking annealing) which can make a steel susceptible to intercrystalline corrosion (which can be detected by special etching).

As may be seen from the curves of Fig. 19.10, steel type 18-9 without titanium or niobium becomes susceptible to intercrystalline corrosion upon heating for 10 minutes at 650-700°C (Fig. 19.10*a*). A similar steel (type 18-10), but additionally alloyed with titanium or niobium is substantially more resisting to intercrystalline corrosion (Fig. 19.10*b* and *c*).

When estimating the results of tests for intercrystalline corrosion it is taken that if a steel is not susceptible to intercrystalline corrosion

[1] The method is ineffective with nitrogen-alloyed steels.

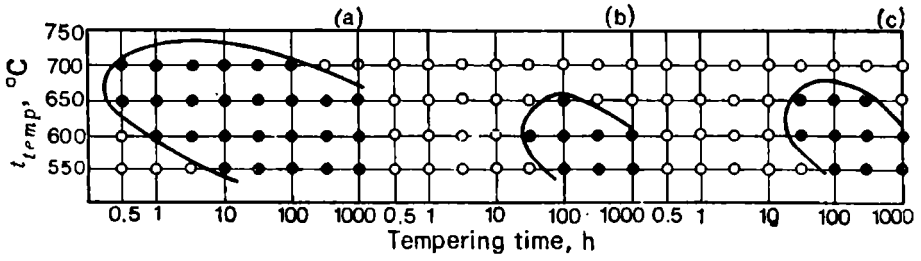

Fig. 19.10. Time of provoking heating to cause intercrystalline corrosion in steel X18H10

(*a*) without stabilizers; (*b*) steel with 0.5% Ti; (*c*) steel with 0.7% Nb. Light dots — no corrosion; black dots — intercrystalline corrosion

upon hardening and tempering for 1 h at 650°C, it can be used in as-hardened state in welded structures and requires no heat treatment after welding.

If a steel turns out to be stable to intercrystalline corrosion on hardening and unstable after provoking tempering (for 1 h at 650°C), it can be used either in non-welded structures or, if welding is unavoidable, should be heat treated (hardened) after welding; otherwise weld seams will not be corrosion-resisting.

Another series of C-shaped curves (Fig. 19.11) shows the effect of carbon and nickel on the susceptibility of austenitic Cr-Ni steels to intercrystalline corrosion. Among the principal alloying elements, these two elements affect most strongly the susceptibility of austenitic stainless steels to intercrystalline corrosion. Carbon can accelerate substantially the precipitation of carbides and thus make a steel liable to intercrystalline corrosion. For that reason the content of carbon in modern stainless steels is limited at 0.03 per cent and sometimes at 0.02 or even 0.015 per cent. With such a low carbon content[1], intercrystalline corrosion can appear only after a very long heating (at 0.03% C) or does not appear at all (at 0.005% C).

Nickel lowers the solubility of carbon in austenite (Fig. 19.8) and makes the austenite less saturated upon hardening, but nonetheless increases the susceptibility to intercrystalline corrosion (Fig. 19.11), since it accelerates the diffusion of carbon, so that the carbide phase precipitates more quickly on grain boundaries.

Purely austenitic steels are also susceptible to another type of corrosion failure which is called *corrosion cracking*, or *stress-induced corrosion*. The phenomenon essentially consists in the following. If a specimen or a steel part which is under load or in which there are residual internal stresses (for instance, due to strain hardening) is placed in a relatively weak corrosive medium, fine cracks can form in its surface; these pass mainly through the body of grains.

[1] Production of steels with such a low carbon content is associated with considerable difficulties.

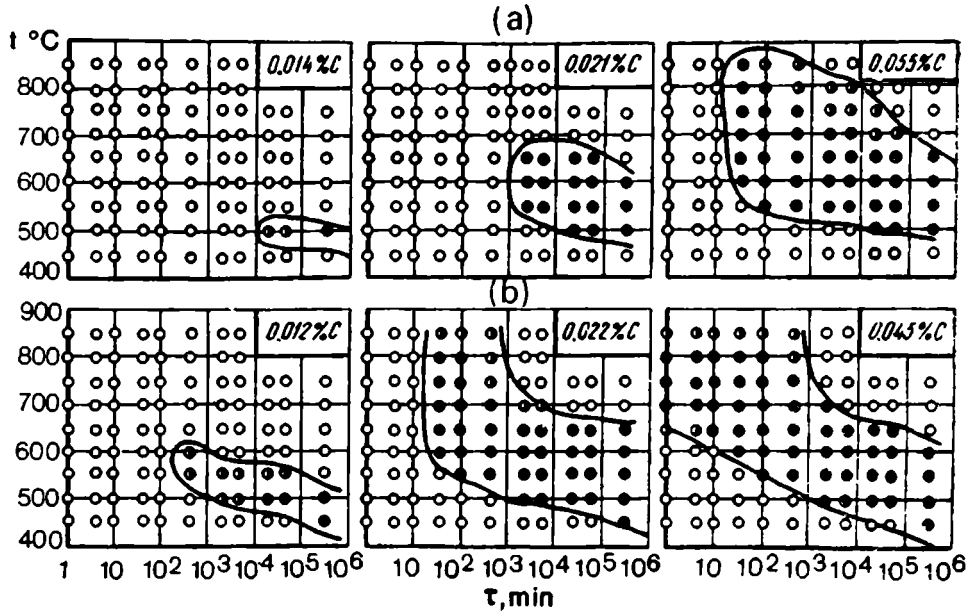

Fig. 19.11. Susceptibility of austenitic Cr-Ni steels with various contents of carbon and nickel to intercrystalline corrosion (the author)

(*a*) 9% Ni; (*b*) 19% Ni. Light dots — not susceptible to intercrystalline corrosion; half-shaded dots — slightly susceptible; black dots — very susceptible

Ferritic stainless steels are also liable to this type of failure, though to a lesser extent. Two-phase (austenite-ferritic) steels are less susceptible to corrosion cracking.

It may be assumed that a crack which has appeared in austenite stops upon reaching the second phase (ferrite). Stress-induced formation of martensite increases the effect of corrosion cracking. This explains why steels with unstable austenite have a low resistance to corrosion cracking. Steels with 30-40% Ni are insensitive to corrosion cracking.

Austenitic stainless steels are used very widely owing to their high process and mechanical properties, as well as to the high corrosion resistance. They can be easily rolled in the hot and cold state, deep-drawn in the cold state, and can be welded by electric welding without the risk of embrittlement of the weld zone.

Heat treatment of austenitic-class stainless steels is quite simple and consists in water quenching from 1 050-1 100°C. Heating to these temperatures causes dissolution of chromium carbides ($M_{23}C_6$) and fast cooling in quenching fixes the state of supersaturated solid solution. Slow cooling in hardening is inadmissible as it may result, as in tempering, in the precipitation of carbides and, therefore, in poorer values of ductility and corrosion resistance. In addition, hardening is associated with recrystallization processes which eliminate the effects of the prior plastic deformation often employed with austenitic stainless steels. The hardness of austenitic stainless

steels decreases on hardening (instead of being increased, as in most other steels) and therefore, hardening is a softening procedure as applied to these steels.

The mechanical properties of austenitic stainless steels in as-hardened (softened) state can be characterized by low values of yield limit and ultimate strength and a very high ductility.

The mechanical properties of selected austenitic stainless steels are given in Table 19.4.

Table 19.4. Mechanical Properties of Austenitic Steels (as Hardened)

Steel Grade	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %	ψ, %	Steel Grade	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %	ψ, %
04X18H10	45	18	40	60	10X14Г14H3T	60	25	35	50
08X18H10	48	20	40	55	12X17Г9AH4	65	30	35	50
12X18H10	50	20	40	55	15X17AГ14	80	40	30	45
17X18H9	58	22	40	50					

Among these steels, steel Grade 04X18H10 naturally has the highest ductility and the lowest strength since it is very low in carbon and contains no other alloying elements except for Cr (18%) and Ni (10%) which are needed to make the steel corrosion-resisting (chromium) and form an austenitic structure in it (nickel).

The strength of steels in this group increases with heavier alloying (carbon and nitrogen have a greater effect than metallic alloying elements). The strongest steels in this group, which are alloyed with carbon and nitrogen, have a yield limit of 25-40 kgf/mm² and an ultimate strength of 60-80 kgf/mm², but are susceptible to intercrystalline corrosion and embrittlement at high temperatures.

A radical method for strengthening austenitic steels is cold strain hardening: a deformation of 80-90 per cent can increase the yield limit up to 100-120 kgf/mm² and the ultimate strength up to 120-140 kgf/mm² with a sufficiently high ductility maintained.

The method is naturally only applicable with thin sheets, strips, wire and the like products.

As we have seen, heat treatment of austenitic-class steels is quite simple and does not affect the mechanical properties. On the other hand, the heat treatment conditions for the intermediate class of austenite-martensitic steels may have an appreciable effect on the steel strength, since they change substantially the structural state. The conditions of heat treatment of these steels are rather complicated.

Stainless steels of this class are mainly applied as high-strength steels. The highest strengthening effect is obtained when their structure is austenite + + temper martensite.

This structural state can be obtained by the heat treatment as follows: hardening to austenite + sub-zero treatment + tempering (ageing). The sub-zero treatment transforms approximately 40 per cent of the austenite into martensite (the M_s point should be near 0°C); tempering at 450-500°C increases

the ultimate strength owing to precipitation hardening which mainly occurs in the α-phase.

Let us see how the mechanical properties of steel Grade X15H9IO vary with changes in the structural state at various stages of heat treatment.

The structure of the steel upon hardening from 1 000°C is 100 per cent austenite and its mechanical properties are as follows[1]: σ_t = 90 kgf/mm², $\sigma_{0.2}$ = = 25 kgf/mm², δ = 30 per cent, ψ = 65 per cent, and a_{n_1} = 30 kgf m/cm².

The structure upon sub-zero treatment at —70°C (after the hardening from 1 000°C) is 40 per cent martensite and 60 per cent austenite and has the following mechanical properties: σ_t = 110 kgf/mm², $\sigma_{0.2}$ = 90 kgf mm², δ = 25 per cent, ψ = 60 per cent, and a_{n_1} = 15 kgf m/cm². The subsequent tempering at 500°C gives a structure of 40 per cent martensite (aged martensite in which the precipitated phase cannot however be revealed) and 60 per cent austenite with the mechanical properties as follows: σ_t = 130 kgf/mm², $\sigma_{0.2}$ = 110 kgf mm², δ = 20 per cent, ψ = 50 per cent, and a_{n_I} = 10 kgf m/cm².

The martensitic transformation can also be induced in this steel by plastic deformation or by hardening from 800°C. In the latter case the martensitic point rises from 0° to +80°C (compared to the state on hardening from 1 000°C), with approximately 30 per cent of martensite being formed on cooling to room temperature. In this case, tempering (ageing) is also needed. The mechanical properties obtained by this method of heat treatment are noticeably lower than those obtained during sub-zero treatment.

The conditions of heat treatment for austenite-martensitic steels and the mechanical properties obtained are given in Table 19.5.

Table 19.5. Mechanical Properties of Austenite-martensitic Stainless Steels

Steel Grade	Heat-treatment conditions, °C			σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %	ψ, %	a_{nI}, kgf m/cm²
	hardening	freezing	tempering + ageing					
08X15H8IO	975	—	—	90	25	30	65	30
	975	—70	—	110	90	25	60	15
	975	—70	500	130	110	20	50	10
09X17H7IO	1 050	—	750+550	90	70	10	40	5

Comparing the data of Tables 19.4 and 19.5, it may be seen that precipitation-hardening austenite-martensitic steels possess substantially higher mechanical properties than purely austenitic steels and should be preferred in all cases where no special requirements are imposed upon the magnetic properties[2].

Steels of the austenite-ferritic class (also called sometimes two-phase steels) are employed less frequently than the two classes discussed, i.e. austenitic and austenite-martensitic steels. The point is that these steels exhibit a great instability in their properties: even slight variations in the composition (within the

[1] The properties typical of the austenitic state; the ultimate strength has been raised owing to partial $\gamma \rightarrow \alpha''$ transformation that has taken place during tensioning of test specimens.

[2] It should be recalled that all austenitic steels are non-magnetic and austenite-martensitic steels, magnetic.

limits of a steel grade) can result in substantial changes in the content of γ- and α-phase, and therefore, in wide variations of the properties.

In addition, these steels are susceptible to embrittlement (at 400-600 C). In the ultimate strength, they excel purely austenitic steels, but this is not advantageous in many applications.

As follows from the foregoing, three principal types of corrosion failure can occur in stainless steels:

(a) general corrosion which develops uniformly over the whole surface and into the depth of metal;

(b) intercrystalline corrosion, and

(c) corrosion cracking.

The rate of general corrosion is measured in linear units (mm/year) and is determined according to a five-index scale:

Index	I	II	III	IV	V
Corrosion rate, mm/year	0.1	0.1-1	1-3	3-10	>10

If the rate of corrosion is less than 0.1 mm/year (index I), the thickness of a stainless steel sheet will diminish by less than 1 mm in 10 years. In that case the metal can be regarded to be corrosion-stable in this medium, since practically it can operate in equipment for a few years without replacement. With a corrosion stability of index II, the metal can be regarded to be limitedly corrosion-resisting and its operation time is usually limited to one year. With an index of III to V, the metal is corrosion-unstable and is unsuitable for operation in the given medium.

The rate of all three types of corrosion failure depends on the composition and structure of steel.

The main factor that determines the resistance to general corrosion is the chromium content. Most austenitic stainless steels contain approximately 18% Cr and have nearly the same corrosion resistance; steels with 14% Cr have a poorer and those with 21% Cr, a better corrosion resistance.

Intercrystalline corrosion depends on carbon content and on the presence of stabilizing elements. Steels low in carbon (<0.03% C) and also those alloyed with titanium or niobium have a rather high resistance to intercrystalline corrosion. Intercrystalline corrosion in these steels can be provoked by tempering at 600-700°C with a holding time of more than 1 h. Steels with more than 0.03% C or those without these elements become susceptible to intercrystalline corrosion on tempering at 600°C with a holding time less than 1 h.

As has been noted, intercrystalline corrosion consists in the precipitation of a carbide network on the grain boundaries. Even if there is no highly aggressive medium, the precipitation of carbides on the grain boundaries adversely affects the ductility of the metal.

Corrosion cracking occurs more quickly if the austenite is unstable to $\gamma \rightarrow \alpha'$ transformation. Its stability can be increased by

increasing the content of austenite-forming elements; the metal can thus be made more resistant to corrosion cracking.

The above considerations can be resorted to when selecting a suitable grade of stainless steel for a particular application.

The most popular grades of stainless steel are given in Table 19.3.

Steels Nos. 1-12 and 14-18 have roughly the same resistance to general corrosion; Nos. 13, 20 and 21 have a reduced resistance, and Nos. 19 and 22-24, an elevated resistance. Steels Nos. 4, 8, 10-12, and 13 have a high resistance to intercrystalline corrosion. Other steel grades have a lower resistance to intercrystalline corrosion, but are only slightly susceptible to corrosion embrittlement.

Steels of the type 18-12 excel the other steels in their resistance to corrosion cracking, and type 18-9 is the poorest in this respect.

Stainless steels are alloyed with molybdenum and copper to increase their resistance in acids and for that reason steels of the types Cr-Ni-Mo and Cr-Ni-Cu-Mo will be discussed in the section on acid-resisting steels.

Selenium and tellurium are added to stainless steels to improve their machinability. Steel No. 6 (X18H10E) is a free-cutting stainless steel.

19.3. ACID-RESISTING STEELS AND ALLOYS

The industrial apparatuses and plants for the manufacture of synthetic non-metallic materials (plastics, glass fibres, etc.) employ aggressive acid media, mostly sulphuric, hydrochloric, nitric and phosphoric acids and their mixtures in various concentrations and at various temperatures.

The stainless steels discussed in the previous section are insufficiently stable in these acids and in other highly aggressive media.

Special *acid-resisting steels* and *alloys* have been developed for operation in these media.

An elevated resistance to the action of acids (resistance to general corrosion) is obtained by alloying austenitic steels with molybdenum and especially with molybdenum and copper, with simultaneous increase in the nickel content (steels of the types Cr-Ni-Mo and Cr-Ni-Mo-Cu, see Table 19.3).

When it is needed to have a high acid resistance (at a level comparable with steel 0Н1943) and at the same time high mechanical properties ($\sigma_t > 100$ kgf/mm^2), it is recommended to use a Cr-Ni-Mo-Cu-Ti-Al alloy; the last two elements in its composition cause intermetallic strengthening, i.e. precipitation of disperse phases of the type $Ni_3(Ti, Al)$.

A higher corrosion resistance is exhibited by nickel-base alloys of the *Hastelloy* type which contain approximately 80% Ni and 20% Mo and are additionally alloyed with some other elements.

The highest resistance to acids is shown by high-melting metals (molybdenum, niobium and tantalum).

Let us consider the resistance of various alloys to acids.

Sulphuric acid. All austenitic stainless steels have a high resistance to this acid at room temperature (except for steels of the X17 type). At the temperatures about 70°C, austenitic Cr-Ni steels are unstable even in acid solutions of a weak concentration, but those alloyed with molybdenum and copper (steel type ЭИ943, see Table 19.3) can operate reliably in the concentrations up to 5% H_2SO_4. All the steels, including type ЭИ943, are unstable in the boiling solutions of sulphuric acid in the concentrations up to 30 per cent; in such cases use should be made of Hastelloy alloys. Finally, only high-melting metals can operate in boiling sulphuric acid in the concentrations from 30 to 60-80 per cent (Fig. 19.12).

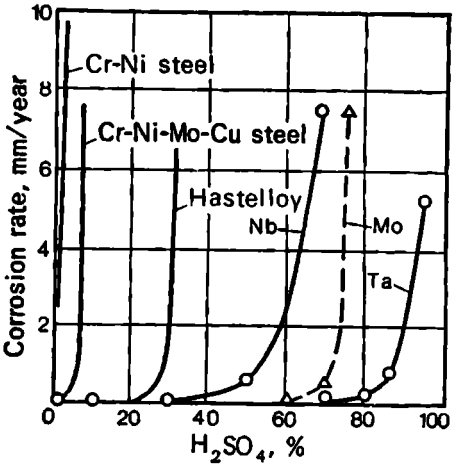

Fig. 19.12. Corrosion rate of various metals in boiling sulphuric acid

Phosphoric acid. Austenitic steels are stable in phosphoric acid in any concentration at room temperature; chromium steels are not stable.

Steel type ЭИ943 is stable in hot (70°C) phosphoric acid in the concentrations up to 25 per cent. Hastelloys are stable in boiling acid (in the concentrations up to 20-50%). At higher concentrations of acid in a boiling solution, high-melting metals should be used.

Hydrochloric acid. Steel type ЭИ943 is the sole steel grade that is stable in diluted (5%) hydrochloric acid at room temperature.

Hastelloy-type alloys can operate in boiling hydrochloric acid in the concentrations up to 20 per cent and high-melting metals, in any concentration.

The compositions of selected alloys of Hastelloy type are given in Table 19.6.

Table 19.6. Composition of Hastelloy-type Nickel-base Alloys, %

Alloy Grade	C	Si (maximum values)	Mn (maximum values)	Mo	Cr	W	V	Co	Fe
Hastelloy B	0.05	1.0	1.0	26-30	1.0	—	0.35	2.5	4.6
ЭП496 (Н70МЦ)	0.05	0.2	0.5	25 29	⩽0.3	—	1.4-1.7	—	⩽4.0
Hastelloy C	0.08	1.0	1.0	15-17	14.5-16.5	3-4	0.35	2.5	4-7
ЭП567 (ХН65МВ)	0.03	0.15	1.0	15-17	14.5-16.5	3.0-4.5	—	—	⩽1.0

All alloys of Hastelloy type contain 15-30% Mo and 60-80% Ni and are also alloyed with cobalt and sometimes with other elements. Their carbon content should be as low as possible, since there is no other means for combatting intercrystalline corrosion than to minimize the content of carbon.

Apart from being highly corrosion-resisting, Hastelloy-type alloys possess high mechanical properties ($\sigma_t > 90$ kgf/mm^2, $\sigma_{0.2} > 40$ kgf/mm^2) and a high ductility, which makes them a valuable structural material. Their mechanical properties can be improved (up to $\sigma_t \approx 120$ kgf/mm^2) by the heat treatment such as employed with heat-resisting nickel alloys, i.e. hardening + ageing at 800°C. The highest strengthening effect corresponds however to the minimum of corrosion resistance, because of which heat treatment can be disadvantageous in some cases.

On the use of high-melting metals for acid-resisting applications see in Ch. 22.

19.4. CRYOGENIC STEELS AND ALLOYS

Steels and alloys for operation at low (sub-zero) temperatures are divided into two groups. The first group is intended for use at low climatic temperatures (to —60°C) in northern regions. The second group is employed in a wide temperature range from room temperature to —80°C or even almost to the absolute zero (4.2K, the boiling point of liquid helium); this group of steels, which are most often austenitic stainless steels, is called *cryogenic steels*. They are used in machines and equipment for the manufacture, transport and storage of liquefied gases, and therefore, have to operate at temperatures near the boiling points of these gases (—183°C for oxygen, —196°C for nitrogen, —247°C for neon, —253°C for hydrogen, and —269°C for helium). They are also employed for processing of liquefied hydrocarbons (methane, butane, etc.) whose boiling points lie within the range from —80° to —180°C.

As other structural materials, cryogenic steels should have an adequate mechanical strength. The specific feature is however that they should operate in the wide temperature range from room temperature to the boiling point of helium, in which their properties may vary substantially.

It may be noted that the strength generally increases with lowering temperature, while the values of ductility and toughness become lower. Hence, a cryogenic steel should have a guaranteed strength at room temperature (since its strength at lower temperatures will be surely higher) and the guaranteed values of ductility and toughness at the lowest temperature of operation.

Though the strength of steel (σ_t, $\sigma_{0.2}$) generally increases at lower temperatures, it can be affected considerably by some other factors associated with phase transformations or with a change in the type of fracture.

Figure 19.13 shows the effect of temperature on the strength properties of austenitic steels (this type of steel is the most common among cryogenic steels). Steel Grade X18H20 (Fig. 19.13*b*) in which the austenite is stable, undergoes no transformations at the low temperatures of deformation and has a ductile fracture. The curves of variation of σ_t and $\sigma_{0.2}$ for this steel are equidistant and their ratio is almost the same at all temperatures ($\sigma_{0.2}/\sigma_t = 0.5$).

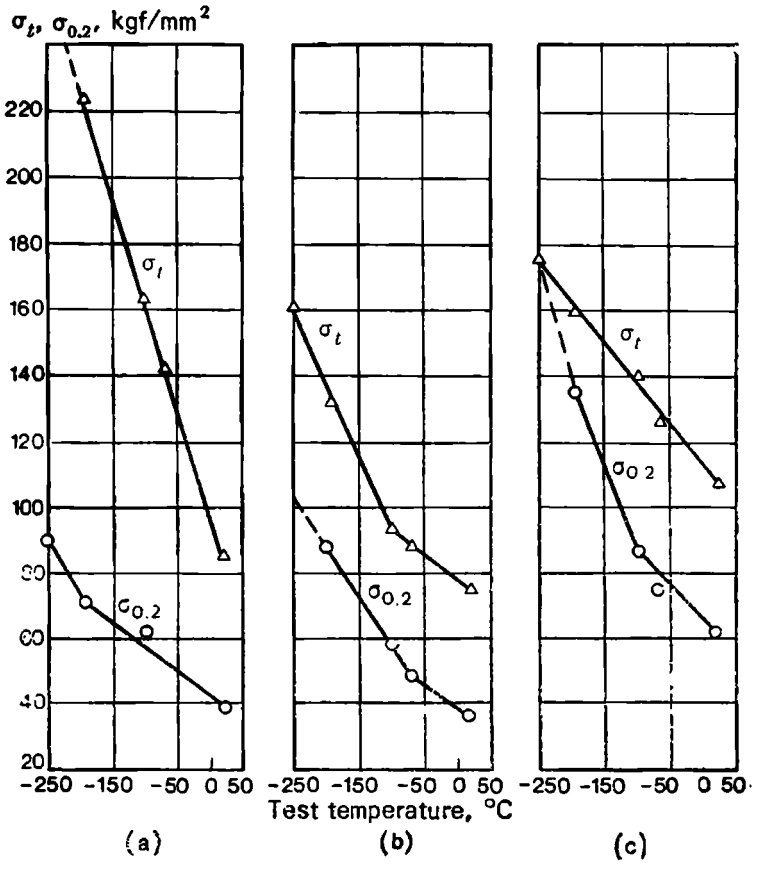

Fig. 19.13. Ultimate strength and yield limit (in notched specimens) of austenitic steels at various test temperatures

(*a*) X18H10; (*b*) X18H20; (*c*) X18АГ19 (the author)

In steel Grade X18H10, as we know (see Sec. 19.2), deformation causes the martensitic ($\gamma \rightarrow \alpha''$) transformation which occurs through plastic deformation, i.e. at stresses exceeding $\sigma_{0.2}$. The value of $\sigma_{0.2}$ of this steel varies as in a steel with stable austenite, but the fracture (at σ_t) occurs in the austenite-martensitic, rather than in austenitic state. Thus, σ_t of this steel is directly proportional to the amount of martensite formed in its structure.

Thus, when martensite forms in the steel structure, the curves for σ_t and $\sigma_{0.2}$ diverge (Fig. 19.13*a*) and the $\sigma_{0.2}/\sigma_t$ ratio decreases. Steel Grade X18АГ19 contains no nickel and, despite its austenitic structure, a brittle component appears in its fracture at the temperatures below —80° or —100°C. The ductility of the steel decreases and the ductile-to-brittle transition point increases quickly as the temperature lowers, the curves of σ_t and $\sigma_{0.2}$ converge (Fig. 19.13*c*) and the ratio $\sigma_{0.2}/\sigma_t$ increases from 0.5 to unity.

Table 19.7 gives the mechanical properties of three types of austenitic cryogenic steel. As may be seen from the table, their strength values (σ_t and $\sigma_{0.2}$) at +20° and —253°C differ widely, and therefore, strength calculations of cryogenic structures should be made for the room temperature at which the strength values are the lowest.

Austenitic Cr-Ni steels have a high impact toughness (a_nI > 20 kgf m cm^2) at room temperature and, since their fracture is tough over the whole tempe-

Table 19.7. Mechanical Properties of Cryogenic Austenitic Steels

Steel Grade	Testing temperature, °C	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	$\sigma_{0.2}/\sigma_t$
X18H10	20	70	25	0.35
	−253	190	45	0.24
X18H20	20	55	27	0.55
	−253	125	60	0.52
X13AГ19	20	80	38	0.48
	−253	130	95	0.72

rature range from room temperature down to the boiling point of liquid hydrogen (−253°C), their impact toughness decreases monotonously with temperature and is still quite high (above 10 kgf m/cm²) at −253°C, evidently owing to the monotonous rise in the strength (Fig. 19.14). For that reason austenitic steels are mainly used at low temperatures (below −196°C), whereas less expensive steels of other types can be used at temperatures above −196°C (i.e. in the range from −80° to −160°C).

As has been shown, nickel is effective in lowering the ductile-to-brittle transition temperature of iron, and therefore, its effect can be used to make iron-nickel (low-carbon) alloys with various values of the ductile-to-brittle transition point (Table 19.8).

The ductile-to-brittle transition point is given in that table as determined by the appearance of brittle portions in a fracture ($90\%B$), i.e. the upper value for a normalized steel is given.

It should be remembered that the impact toughness of all the steels is approximately the same (a_{nI} = 27-30 kgf m/cm²) at that temperature.

As may be seen from Table 19.8, nickel increases the strength properties (σ_t), lowers the ductile-to-brittle transition point (T_{50}), and therefore, increases the impact toughness at −196°C.

For the steels with 6 and 9% Ni in the table, the lower line gives higher values of properties which are obtained by a special heat treatment procedure—double normalizing (at 900°C and at 790°C) followed by tempering at 560°C.

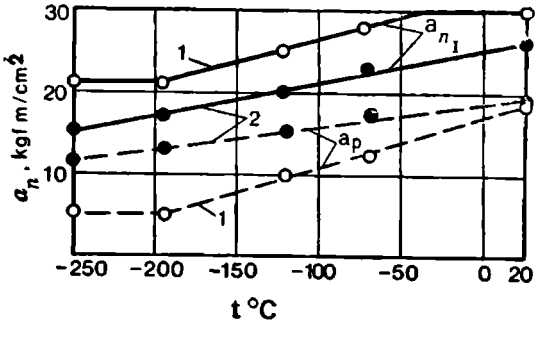

Fig. 19.14. Impact toughness of austenitic steels

1 — X18H20; *2* — X18H10

Since nickel is deficient, nickel-alloyed steels should be selected carefully according to their application. The criterion is the ductile-to-brittle transition point which is determined as T_{50} (50 per cent of brittle component allowed in the fracture) for parts not to be subjected to impact loads and as T_{90} for dynamically loaded parts (i.e. no brittle component is practically allowed in their fracture).

Therefore, steel type 0H6 (with 6% Ni) can be used at temperatures

Table 19.8. Effect of Nickel on the Mechanical Properties and Ductile-to-brittle Transition Point of Iron (0.05% C)

Ni, %	Ductile-to-brittle point, °C		Mechanical properties		Ni, %	Ductile-to-brittle point, °C		Mechanical properties	
	T_{90}	T_{50}	σ_t at +20°C, kgf/mm²	a_{n_I} at −196°C, kgf m/cm²		T_{90}	T_{50}	σ_t at +20°C, kgf/mm²	a_{n_I} at −196°C, kgf m/cm²
0	0	−40	42	0.5	6	−100	−180	60	8.0
1	−20	−60	45	1.0		−180	−196	57	12
2	−40	−90	50	1.5	7	−120	−196	60	12
3	−50	−120	50	2.3	9	−130	−196	65	12
4	−70	−140	52	3.1		−180	−196	62	24
5	−90	−150	55	3.8					

down to −100°C in dynamically loaded parts and down to −180°C in those not subjected to dynamic loads (practically it can be used at temperatures down to −196°C, the 'oxygen' temperature). Steel type 0H9 (with 9% Ni) can be used respectively at −130° and −196°C. The 'hydrogen' and 'helium' temperatures (−253°C and −269°C) are evidently too low for these steels. Further, these steels are not corrosion-resisting.

Table 19.9. Composition and Properties of Selected Cryogenic Steels

Steel Grade	Structure	Ductile-to-brittle transition point		Mechanical properties	
		T_{90}	T_{50}	σ_t at +20°C, kgf/mm²	a_{n_I} at −196°C, kgf m/cm²
0H6	Ferrite	−100	−180	55	8
0H9	Ditto	−130	< −196	65	12
10Х14Г14Н4Т	Austenite	−196	< −196	65	20
10Х18Н10Т	Ditto	< −196	< −196	55	20
07Х21Г7АН5 (ЭП222)	Ditto	< −196	< −196	70	20
03Х13АГ19	Ditto	50	−196	70	17
03Х20Н16АГ6	Ditto	< −269	< −269	70	20
03Х19Г10Н7АМ2 (ЭП731)	Ditto	< −196	< −196	80	10
03Х13Н9Д2ТМ (ЭП699)	Austenite + + martensite	< −196	< −196	110	6

If a high corrosion resistance is also needed[1], use should be made of the austenitic Cr-Ni steels discussed in Sec. 19.2; they have a higher cold resistance than ferritic-structure steels (as types 0H6 and 0H9).

Since austenitic stainless steels have a relatively low strength, high-strength cryogenic steels have been developed such as steel ЭП222 with $\sigma_{0.2}$ = 40 kgf/mm² and ЭП699 with $\sigma_{0.2}$ = 80 kgf/mm². They are however rather high in nickel (around 10%) and later efforts were directed on developing low-nickel steels suitable for operation at not so low temperatures. The properties of some most popular grades of cryogenic steels are given in Table 19.9.

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[1] The liquefied gases mentioned above are not corrosion-aggressive.

Chapter 20

WEAR-RESISTING STEELS AND ALLOYS

20.1. WEAR RESISTANCE

The durability of many machine parts and other articles, i.e. their operation for a long time, is in many cases associated with the wear resistance of the material they are made of.

The wear of machine parts may be due to the friction of metallic parts against each other, the eroding effect of liquid and gaseous media, scratching of solid particles on the surface of parts, and other surface phenomena.

The mechanism of wear may be different and depends on the specific conditions of operation of parts, but consists in the general in the detachment of small particles of the material from the surface. In cases of common friction, the surface of the metal is strain hardened and its resistance to abrasion increases. Therefore, the ability of a metal to be strain hardened determines to a large extent the wear resistance. In cases of abrasion wear, i.e. when hard particles of an abrasive material (such as sand) tear off tiniest particles from the metal surface, the resistance to wear is determined by the resistance of the metal to brittle fracture and by its hardness. In aggressive media, the resistance to wear also depends on the corrosion resistance of the material. This is why the wear resistance of an alloy (steel) is determined by the physicochemical properties of the alloy and by the conditions of wear; the latter also determine the optimal structure and properties of the metal.

The resistance to abrasion wear increases with an increase in the hardness of the material, but this relationship is different for various materials (Fig. 20.1), because of which the wear resistance can be increased effectively by surface hardening or other methods for increasing the surface hardness (carburizing, nitriding, etc.). For the same surface hardness, steels having the structure of martensite + carbides have a higher wear resistance than those containing no excess carbides (Fig. 20.1).

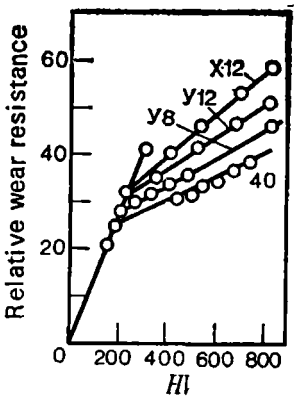

Fig. 20.1. Effect of hardness on wear

For the same hardness, a steel having a coarse-grained structure has a lower wear resistance than a steel with a fine-crystalline structure (since the former has a lower resistance to brittle fracture).

On the other hand, graphite inclusions, which are known to impair the mechanical properties of steels, improve the wear resistance in friction, since they are exposed at the surface as the wear proceeds and break along the cleavage planes into thinnest lamellae which fill in recesses in the friction surfaces and thus prevent dry metal-to-metal friction and seizing. In other words, graphite inclusions serve as a lubricant.

A higher wear resistance can also be obtained by using porous metal-ceramic materials impregnated with oil.

20.2. GRAPHITIZABLE STEEL

Graphitizable (graphitic) steel has a high wear resistance. Graphite can be formed in the steel structure by partial decomposition of cementite, because of which graphitizable steels should be high in carbon and also in silicon (as an alloying addition) which increases the capability of a steel for graphitizing.

The compositions of selected graphitizable (graphitic) steels are given in Table 20.1.

Table 20.1. Composition of Graphitizable Steels, %

Steel Grade	C	Si	Mn	Other elements
ЭИ293	1.50-1.75	0.75-0.95	0.20-0.40	—
ЭИ336	1.50-1.70	0.70-1.00	0.15-0.40	0.4-0.7 Cu
ЭИ366	1.30-1.45	1.60-1.25	0.40-0.50	0.2-0.4 Ti

Note. The steels may contain up to 0.2% Ni, 0.08% Cr, 0.025% S, and 0.03% P.

In cast and hot-rolled state, these steels have the structure of lamellar pearlite with excess carbides (often as a network). The required concentration of graphite in the structure is obtained by graphitizing annealing, with the lamellar pearlite being transformed into a granular form for better machinability. The conditions of graphitizing annealing are in general similar to the graphitizing annealing of malleable cast iron[1] and consist in heating at 820-840°C for about

[1] Because graphitic steels are similar to malleable cast iron in their composition, differing only in a lower carbon content.

5 hours, cooling to 700-720°C, and holding at this temperature for 5-15 hours to allow partial graphitization of the excess cementite. The metal is then cooled to 600°C in the furnace and down from that temperature in the air.

After this heat treatment, the structure of the steel consists of granular pearlite with a certain quantity of fine rounded-off graphite inclusions (Fig. 20.2.)

Graphitized steel parts can be employed in as-annealed state or after hardening and tempering.

Annealed graphitic steel excels in strength the high-strength cast iron and common structural carbon steel (as normalized), but is inferior to the latter as regards the ductility:

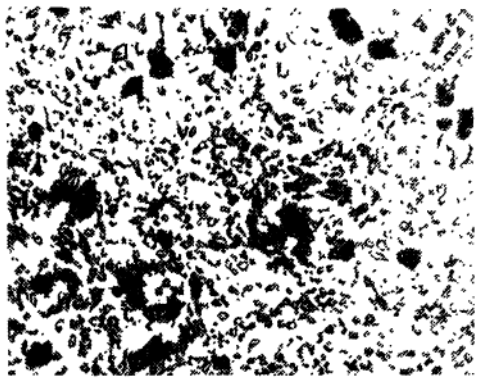

Fig. 20.2. Structure of graphitized steel (granular pearlite + rounded-off graphite inclusions). ×500

	σ_t, kgf/mm²	δ, %
Graphitic steel . . .	85	6
Steel Grade 50 . . .	60	20
High-strength cast iron	40	10

Heat-treated graphitic steel is employed in cold-forming dies, gauges, track shoes and other parts to be subjected to high pressures and wear in operation. In annealed state, graphitic steels are used as substitutes of non-ferrous metals: copper and bronzes.

Graphitic steels are used for casting motor crankshafts. The presence of graphite in the structure improves the capacity of the steel to damp oscillations, while its insufficient strength can be compensated by design measures (since castings can be given a more favourable form than forged parts).

20.3. HIGH-MANGANESE STEEL

As has been noted earlier, a high wear resistance can be ensured by obtaining a high hardness in the surface of metal. There is, however, a type of austenitic steel which has a low hardness (only 200-250 *HB*) but a high wear resistance under the conditions of common friction with large pressures (when there is no purely abrasive wear). This is what is called *Hadfield steel*[1] (Г13) which contains 1.2% C and 13% Mn.

Hadfield steel is employed in as-cast and less frequently in hot-deformed state.

Heat treatment of cast or forged parts made of Hadfield steel (the steel is poorly machinable) consists in water quenching from 1 050-1 100°C. Quick cooling in water inhibits almost completely the precipitation of carbides so that a purely austenitic structure is

[1] Invented by R. A. Hadfield of Britain in 1882.

Fig. 20.3. Microstructure of steel Г13 (austenite) upon hardening from 1 100°C. ×250. Traces of plastic deformation

formed (Fig. 20.3) (which can be ensured at the Mn:C ratio not less than 10%).

Hadfield steel has high values of toughness and ductility typical of austenitic steels and a fairly high strength. Its mechanical properties (on casting and hardening to austenite) are approximately as follows: σ_t = 80-100 kgf/mm², $\sigma_{0.2}$ = 26-40 kgf/mm², δ = 40-50 per cent, ψ = = 40-50 per cent, hardness, 180-220 *HB*.

The plastic properties of the steel are worsened on tempering at 200-300°C owing to the precipitation of carbides.

Hadfield steel has a low hardness but an exceptionally high wear resistance in friction with impacts and shocks. This can be explained by its elevated capacity to strain hardening (Fig. 20.4) which is appreciably higher than in common steels of a comparable hardness.

Austenitic nickel-free steel type Г13, either as-cast or as-forged, has a pronounced ductile-to-brittle transition point (Fig. 20.5), T_{50}, which increases with a higher phosphorus content.

It was assumed at one time that f.c.c. lattice alloys had no ductile-to-brittle transition point and in that connection a high content of phosphorus (up to 0.12%) was allowed in steel Г13. The latest studies have shown however (see Fig. 20.5) that nickel-free f.c.c.-lattice steels, as b.c.c. steels, are susceptible to

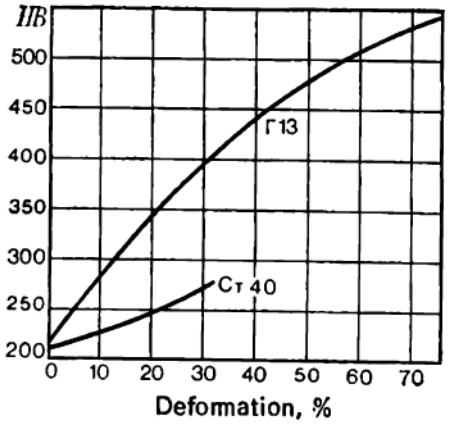

Fig. 20.4. Effect of work hardening on the hardness of carbon steel 40 (*1*) and steel Г13 (*2*)

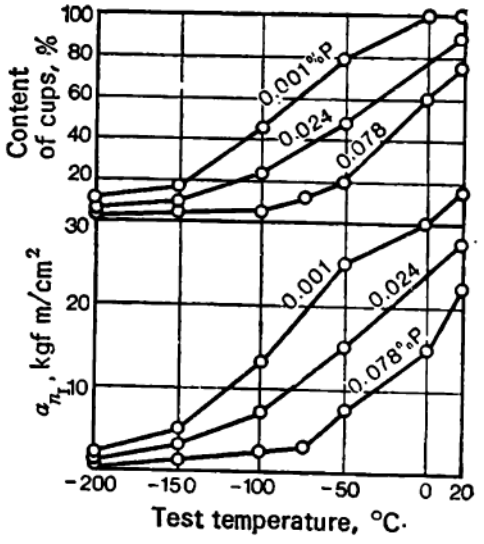

Fig. 20.5. Effect of phosphorus in steel Г13 on impact toughness and the percentage of fibrous fracture (the author)

cold brittleness. This is why the steel Г13 for critical castings should be strictly checked for the content of phosphorus (the allowable phosphorus content is not more than 0.02%).

It was assumed earlier that the high strengthening effect of plastic deformation in the steel was due to the formation of strain-induced martensite. Precise measurements have shown however that only 0.5 to 1.5 per cent of martensite forms even on very heavy deformations and at low temperatures and this quantity of martensite can have no noticeable effect on the steel hardness.

The high strengthening effect in Hadfield steel is due to strain hardening[1]. For the same degree of deformation, mosaic blocks in Hadfield steel are disintegrated more than in other steels, even in austenitic grades. It is still unclear what factors are responsible for these specific properties of high-manganese austenite. Owing to the high toughness of the austenite along with sufficiently high values of strength and wear resistance, Hadfield steel is an irreplaceable material for making parts to be subjected to wear and impact loads.

Hadfield steel is used for making excavator shovels, caterpillar track-shoes, tramline crossings, elements of rock crushers, etc., i.e. elements in which wear is accompanied by heavy impacts and large pressures; with abrasion wear, when there are no large pressures, and therefore, no strain hardening, Hadfield steel has no essential advantages in wear resistance over other steels of the same hardness.

There are special steels having a high resistance to cavitation erosion[2]. They are usually high in chromium (to increase their corrosion resistance) and contain structurally unstable austenite. As has been shown experimentally by I.N. Bogachev the formation of martensite under the impact of water jets has a positive effect on the cavitation resistance. An example of cavitation-resisting steel is Grade 30Х10Г10 (0.3% C, 10% Cr, and 10% Mn).

20.4. HARD-FACING MATERIALS

Steel parts can be made more resisting to wear and worn parts can be restored by hard facing, i.e. depositing a layer of a hard-to-wear material on their surface by welding. Hard-facing materials are prepared in the form of iron-clad rods which are melted by an oxy-acetylene torch or electric arc and are deposited in a liquid (or semi-liquid) state onto the metal surface.

The common materials used for hard facing are usually very hard and wear-resisting, but have a low mechanical strength because of being brittle.

Various types of hard-facing material can be used, for instance a powder mixture of W_2C and WC carbides in a eutectic proportion[3]. The mixture is packed into an iron tube and is melted by some welding technique. The deposited hard-facing layer consists of iron and inclusions of tungsten carbide. This material excels all other hard-facing materials in the hardness and wear resistance, but is very brittle; its ultimate strength in bending is only 30-50 kgf/mm², and that in tension is almost zero.

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[1] Distortions of the crystal lattice, disintegration of mosaic blocks.
[2] The resistance to wear by liquid and gaseous flows.
[3] 4.5% C and tungsten the balance; $T_{m.p.} = 2\,525$°C.

Hard-facing rods are manufactured in various grades with various dispersity of carbide powder (from 20 to 80 mesh).

Another type of hard-facing material is manufactured in the form of rods of an iron-chromium-nickel alloy having a composition of 30% C, 30% Cr, 5% Ni, and 3% Si or 1.7% C, 15% Cr, 2% Ni, and 2% Si, the balance being iron. The former alloy has a higher hardness and a higher brittleness (the hardness values of the two alloys are respectively 50 and 40 *HRC*).

A mechanical mixture of ground ferro-chrome, ferro-manganese, cast iron and coal is also used as a hard-facing material. Upon melting and depositing onto the surface, there forms an alloy (called *Stalinite*) of an approximate composition as follows: 10% C, 20% Cr, 15% Mn, 3% Si and iron the balance. Its structure is austenite + a large quantity of carbides and it has a high hardness (more than 65 *HRC*).

A method of electric-arc hard-facing is employed widely, in which an iron or steel electrode is coated with a mixture of various components to form the desired deposited layer on steel parts.

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Chapter 21

TITANIUM AND TITANIUM ALLOYS

Titanium has very valuable properties: a low density, high strength and high corrosion resistance. This explains the progressively increasing rate of its production and consumption in the world which may be seen from the following data (without the USSR):

Year	1948	1953	1966
Titanium production, tons	2	2 100	22 000

Titanium is used most widely in aircraft and rocket engineering and other branches of industry where a high unit strength is essential. Titanium alloys have the highest values of unit strength (σ_t/γ) in the temperature interval between 300 and 600°C and are only inferior to aluminium alloys at temperatures below 300°C and to iron- and nickel-base alloys at temperatures above 600°C.

Titanium is the fourth among the most common metallic elements found in the Earth (after aluminium, iron, and magnesium). Its content in the Earth's crust is quite high (0.6%). The production of titanium will inevitably grow extensively in the future, though at present it is too expensive to be used widely.

21.1. THE PROPERTIES OF TITANIUM

Titanium is a silvery white metal of a low density (4.5 g/cm^3) and a high melting point (1 672°C).

The properties of titanium depend substantially on its purity. For instance, commercial titanium grades of a purity (% Ti) of 99.99, 99.8, 99.6, 99.5, and 99.4 have the hardness values (HB), respectively, of 100, 145, 165, 195, and 225.

Titanium has two allotropic forms: low-temperature α-modification with a close-packed hexagonal lattice ($a = 2.9$ Å and $c = 4.67$ Å at 20°C) and high-temperature β-modification with a body-centred cubic lattice ($a = 3.31$ Å at 900°C). The temperature of $\alpha \rightleftarrows \beta$ transformation is 882°C.

Titanium is produced as sponge at metallurgical works, which is then remelted at machine-building works into commercial titanium or alloyed with various elements to make titanium alloys.

Titanium sponge is graded with letters ТГ and digits indicating the hardness of standard specimens made of it (for instance, ТГ100, ТГ110, etc.). Therefore, a lower number corresponds to a higher purity of the metal.

Commercial titanium, i.e. the metal made from titanium sponge and scrap, has a rather high content of impurities (see Table 21.1), because of which the

Table 21.1. Impurities in Commercial Titanium, % (Upper Limits)

Titanium Grade	Fe	Si	C	O	H
BT1-0	0.18	0.10	0.07	0.12	0.010
BT1-00	0.12	0.08	0.05	0.10	0.008

Note. Grade BT1-0 may contain up to 0.04% N and up to 0.3% of other impurity elements.

strength of commercial titanium on annealing is around 60 kgf mm², i.e. twice as much as that of the purest iodide titanium. The strength of the metal can be increased by strain hardening[1].

The temperature of recrystallization of titanium at various degrees of deformation is as follows:

Deformation, %	10	25	60
t_{re}, °C	700	550	500

Commercial titanium can be easily forged and welded and is used for making various semiproducts.

21.2. ALLOYING OF TITANIUM

As with iron, of primary importance in the alloying of titanium is the solubility of an alloying element in titanium and the effect of that element on the position of the critical point (the temperature of $\alpha \rightleftarrows \beta$ transformation).

In that connection, all elements can be divided into two groups. Those belonging to group A are completely (or almost completely) soluble in titanium and those of group B are only partly soluble and can, in a relatively low concentration, form compounds with titanium (*titanides*).

Further, alloying elements can either raise or lower the temperature of $\alpha \rightleftarrows \beta$ transformation (and can therefore be divided into two classes: I and II).

For the general estimation of the effect of alloying elements on titanium, it is important to establish how they affect the polymorphous transformations in titanium and what compounds they can form with titanium (i.e. whether they belong to group IA, IB, IIA, or IIB). The answer can be found by reference

[1] A deformation of 40 per cent can raise σ_t of commercial titanium up to 80 kgf/mm².

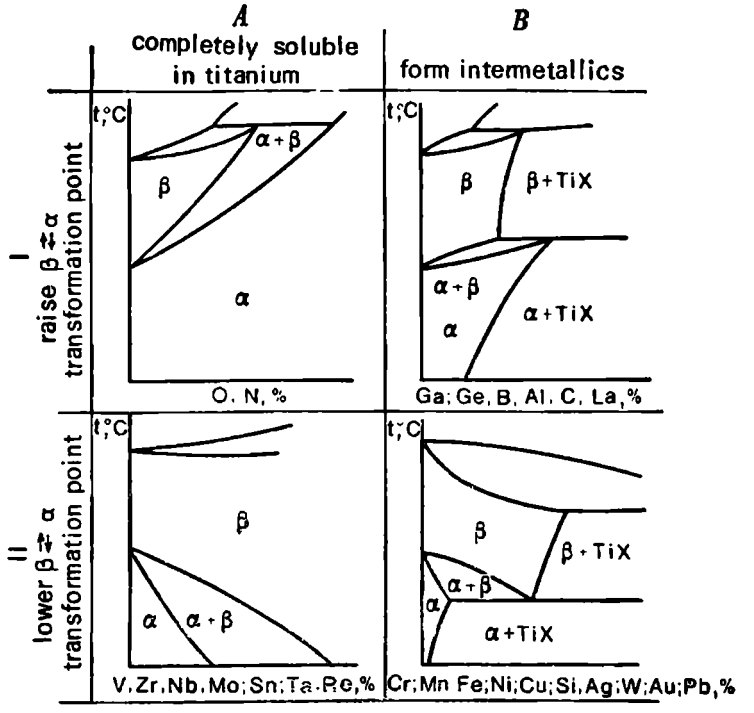

Fig. 21.1. Constitutional diagram of titanium alloys. Classification diagram

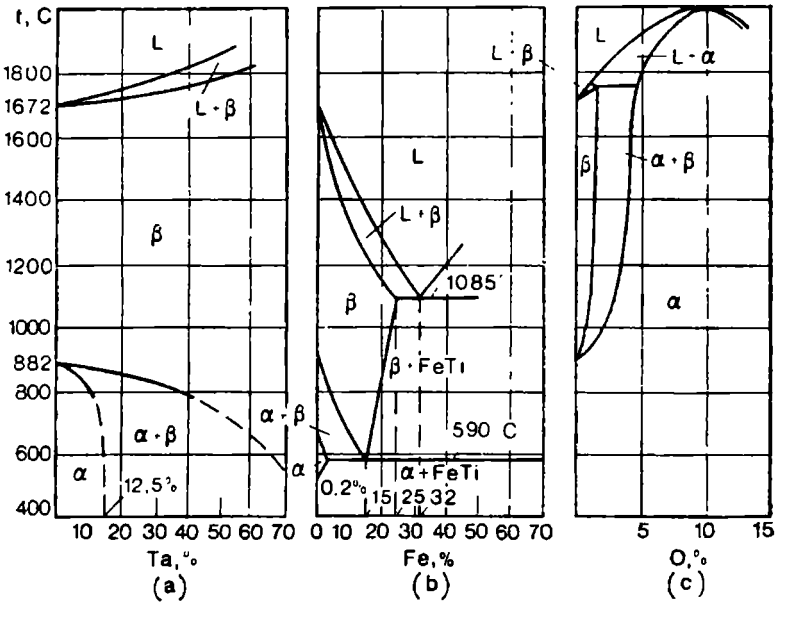

Fig. 21.2. Constitutional diagram of titanium alloys
(*a*) Ti-Ta; (*b*) Ti-Fe; (*c*) Ti-O

to the binary constitutional diagrams 'titanium-alloying element', such as those shown in Fig. 21.1 in the form of a classification scheme.

Figure 21.2 shows the real constitutional diagrams of the systems Ti-Ta, Ti-Fe and Ti-O which relate, respectively, to groups IIA, IIB and IA.

The elements whose atomic radii differ from that of titanium by not more than 12-15 per cent can as a rule form solid solutions in any concentrations with titanium (group A). The elements with a great difference in atomic radii can only form solid solutions in definite concentrations and intermediate compounds of the type of Ti*X* (titanides); they belong to group B.

If an element is isomorphous to α-titanium, i.e. has a hexagonal crystal lattice, it widens the α-region (class I); elements which are isomorphous to β-titanium, i.e. those having a b.c.c. lattice, widen the β-region (class II). The former are called *α-stabilizers* and the latter, *β-stabilizers* (the classification of alloying elements is shown in Fig. 21.1)[1].

21.3. PHASE TRANSFORMATIONS IN TITANIUM ALLOYS

Owing to the existence of the high-temperature β-modification of the solid solution which can be undercooled substantially various structures can be formed in titanium alloys by heat treatment (Fig. 21.3).

The polymorphous $\beta \rightleftarrows \alpha$ transformation can occur by two different mechanisms.

At high temperatures, i.e. at a slight undercooling below the equilibrium temperature of $\beta \rightleftarrows \alpha$ transformation, the latter proceeds by the common diffusion mechanism, whereas at an appreciable undercooling, and therefore, at a low temperature, when the mobility of atoms is low, the transformation takes place by the diffusionless martensitic mechanism. In the former case, a polyhedral structure of α-solid solution is formed and in the latter, an acicular (lamellar) martensitic structure which is usually denoted as α′ (Fig. 21.3*a* and *b*).

The alloying elements which lower the $\beta \rightleftarrows \alpha$ transformation temperature naturally favour the formation of martensite, whereas with slight alloying an intensive cooling would be required. With a very high content of β-stabilizers, the temperature of $\alpha \rightleftarrows \beta$ transformation drops to zero and β-solid solution can be cooled to room temperature without transformation.

As in all other cases, there exists a temperature at which the formation of martensite begins on cooling (point M_s). All β-stabilizers lower the M_s point, as shown in Fig. 21.4.

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[1] The elements which are isomorphous to α-titanium (magnesium, zinc, cadmium, beryllium) cannot be melted together with molten titanium, because of which the constitutional diagrams of their systems with titanium have not been constructed. Alloys of the systems Ti-O and Ti-N can be conditionally related to group IA; they have a wide homogeneous α-region and melt down without decomposition. The constitutional diagrams of these systems should be similar to the diagram IA in Fig. 21.1.

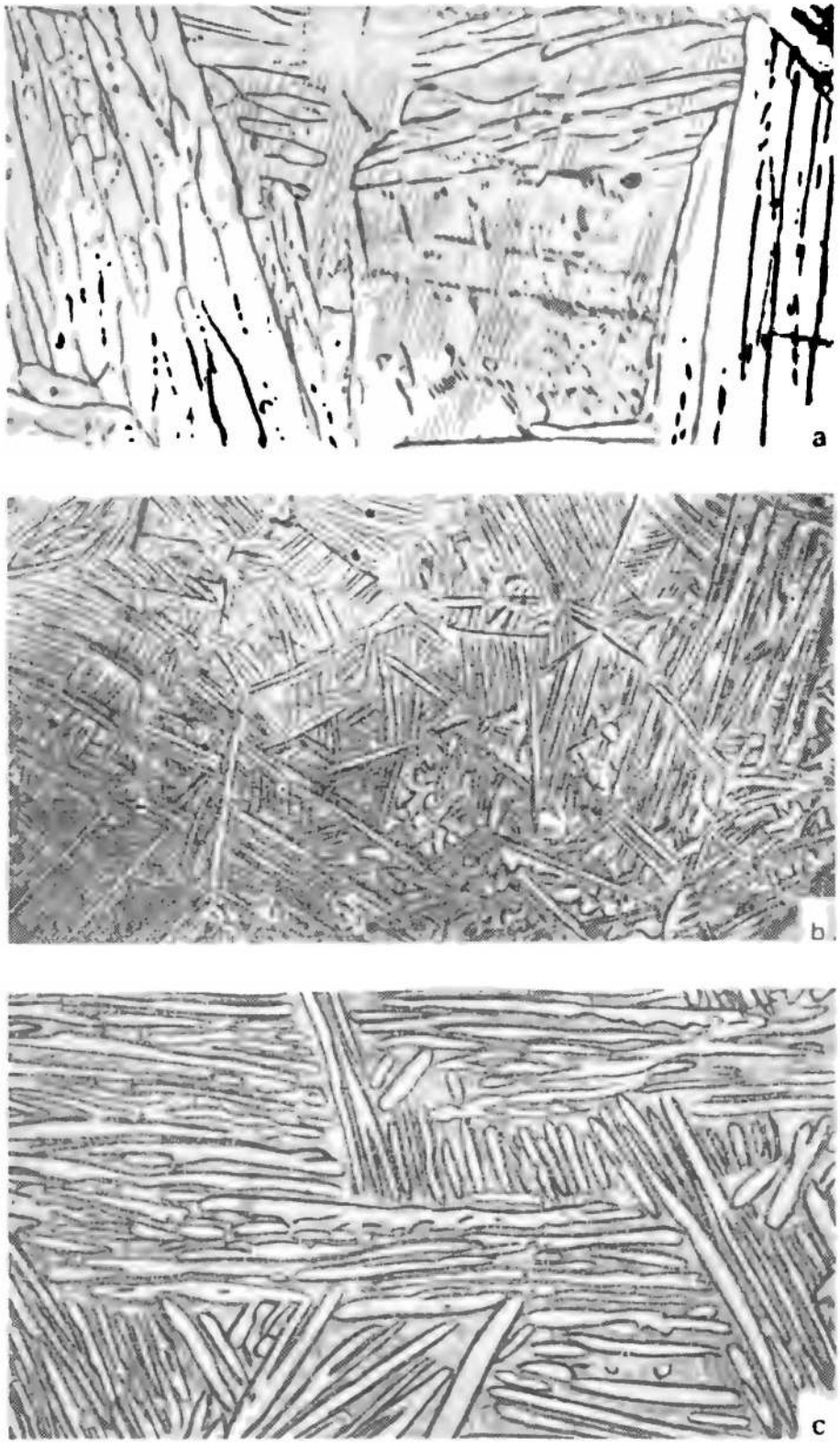

Fig. 21.3. Structures of titanium alloys. ×400

(a) α-solid solution (BT1 alloy); (b) α′-phase (martensite formed by hardening of BT1 alloy from 1 075°C); (c) α+β solid solutions (OT4 alloy)

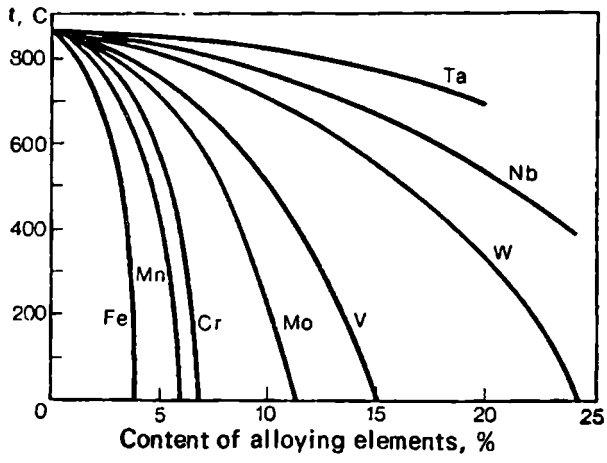

Fig. 21.4. Effect of alloying elements on M_s point in titanium alloys

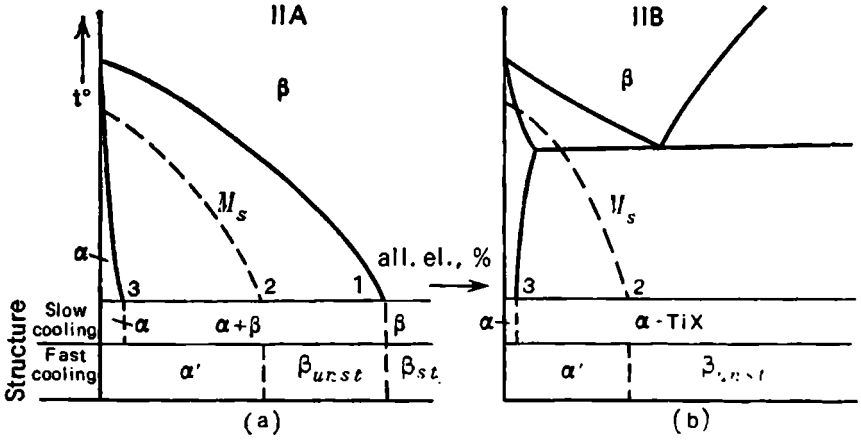

Fig. 21.5. Effect of cooling rate and the content of alloying elements on the structures formed in titanium alloys

The equilibrium diagram (Fig. 21.5) with the line of the beginning of the martensitic transformation superimposed on it[1], shows the structures formed on fast (dotted lines) and slow (solid lines) cooling from the β-region.

A System Having the Constitutional Diagram of Type IIA (Fig. 21.5*a*)

With slow cooling:

(a) the transformation is complete at a low content of alloying elements;

(b) the $\beta \rightarrow \alpha$ transformation is incomplete at a certain average content of the elements, and the alloy contains an equilibrium 'retained' β-phase (Fig. 21.3*b* or *c*);

[1] Figure 21.5 shows the temperature of the beginning of martensitic transformation (M_s), but not the temperature of phase equilibrium of α- and β-solid solutions of the same concentration (T_0).

(c) with the content of an alloying element above a certain value (point *1* in Fig. 21.5*a*), β-phase can be cooled to room temperature without transformation.

With fast cooling:

(a) in alloys of a concentration up to point *2*, the $\beta \rightarrow \alpha$ transformation proceeds by the martensitic mechanism (there form α-phase and retained β-phase between points *2* and *3*);

(b) in alloys of a concentration between points *2* and *1* there forms a β-structure upon hardening; this structure is however unstable and can be transformed by heating;

(c) in alloys of a concentration after point *1*, stable β-phase forms irrespective of whether the cooling has been fast or slow.

A System Having the Constitutional Diagram Type IIB (Fig. 21.5*b*)

During slow cooling, in all alloys except for those of a concentration up to point *3*, β-phase decomposes by the eutectoid reaction $\beta \rightarrow \alpha + TiX$, which is preceded with the precipitation of excess α-phase or titanide (TiX).

On fast cooling, alloys with the concentration of the alloying element below point *2* form martensite by the reaction $\beta \rightarrow \alpha'$ (with retained β-phase in alloys whose concentration is between points *2* and *3*).

Thus, the β-phase in titanium alloys can transform into α-phase ($\beta \rightarrow \alpha$), decompose into eutectoids ($\beta \rightarrow \alpha + TiX$), transform by the martensitic mechanism into α′-phase on an appreciable undercooling, or finally, when the content of a β-stabilizer is high, can be undercooled to room temperature without transformation.

As distinct from Fe-C alloys, the eutectoid mixture in titanium alloys has elevated hardness and brittleness, whereas the titanium martensite (α′) has low values of hardness and ductility and differs only slightly in its properties from the original β-phase.

The crystal structure of α- and α′-phase is practically the same (hexagonal close-packed lattice), but transformations at low temperatures can cause distortions in the α-lattice and diminish the ductility (this type of martensite in titanium alloys is sometimes denoted as α″).

Since the transformation of β-phase is determined by the degree of undercooling, the nature of the transformation can be described by means of the diagram of isothermal decomposition of that phase.

Let us take, as examples, two diagrams of isothermal decomposition of β-phase* in Ti-Mo alloys with 2 and 8% Mo (Fig. 21.6). The Ti-Mo system relates to type IIA. With the low content of Mo (2%), the martensitic transformation lies in the temperature range between 780° (M_s) and 650°C (M_f) (shown hatched in the figure). Above point M_s, the $\beta \rightarrow \alpha$ transformation proceeds by the common reaction and in the range from 780 to 650°C, by the martensitic mechanism. Below 650°C, the curve describes the process of martensite tempering ($\alpha' \rightarrow \alpha$) in which β-phase is retained.

In an alloy with 8% Mo, the martensitic transformation occurs in the temperature range from 350 to 200°C. At higher temperatures, there are two regions of various transformations: the normal $\beta \rightarrow \alpha$ transformation in the temperature interval of 800-500°C (with a substantial quantity of β-phase being retained in the structure of a given alloy) and the formation of α-phase via an intermediate ω-phase (by the reaction: $\beta \rightarrow \omega \rightarrow \alpha$) in the temperature interval of 500-350°C. It should be noted that the hexagonal ω-phase is brittle and can impair the mechanical properties of an alloy.

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* Or α′-phase upon tempering.

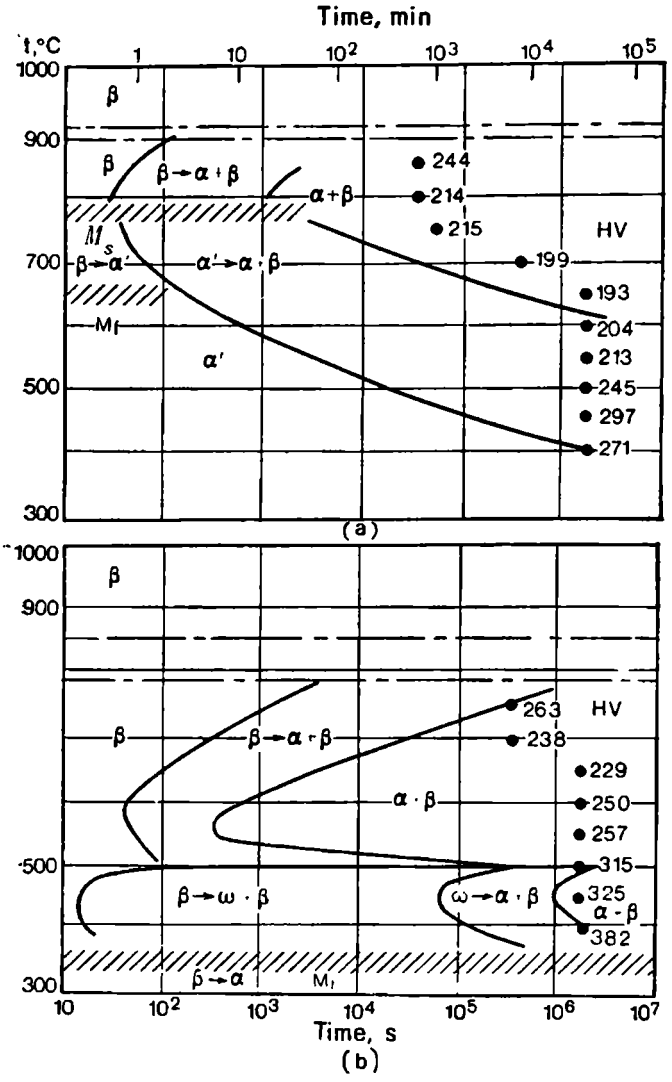

Fig. 21.6. Diagram of isothermal decomposition of β-phase in titanium alloys with various content of molybdenum

(*a*) 2% Mo; (*b*) 8% Mo

During tempering, the α'-phase transforms into polyhedral α-phase (see Fig. 21.6); in some alloys, the retained unstable β-phase can transform into ω-phase at 300-500°C, which can impair the mechanical properties of alloys.

21.4. COMMERCIAL TITANIUM ALLOYS

As in the classification of alloy steels (see Sec. 15.1), titanium alloys are classified by the structure they have after cooling (normalizing) in air and are accordingly divided into α-, α + β-, and β-alloys.

Modern commercial α-alloys have a relatively low plasticity and

are not embrittled during heat treatment. This class of alloys includes pure titanium and its alloys with aluminium.

Among titanium alloys, β-alloys have the highest plasticity and the least strength; they undergo no phase transformations during heating[1].

Alloys of the α + β type have a higher strength than single-phase alloys, can be easily forged, stamped, and heat treated, and are embrittled only on particular heat treatment conditions (the appearance of ω-phase).

The two-phase α + β structure is formed at a definite content of β-stabilizers[2]; α + β-alloys are best suitable for practical applications. Most of commercial titanium alloys belong to this class.

The compositions of selected commercial titanium alloys and the guaranteed mechanical properties (without special heat treatment) are given in Tables 21.2 and 21.3.

Titanium alloys have a normal modulus of elasticity of 115 000 kgf/mm², Poisson's ratio of 0.3, density of 4.5 ± 0.1 g/cm³, electric resistivity 1.0-1.6 ohm mm² m, coefficient of linear expansion 8.0×10^{-6}-8.6×10^{-6} mm/(mm °C), and heat conductivity 0.02 cal/(cm s °C).

As follows from Table 21.2, all commercial titanium alloys contain roughly

Table 21.2. Composition of Commercial Titanium Alloys, %

Alloy Grade	Al	Mn	V	Mo	Cr	Si	Other elements
				α-alloys			
BT5	4.3-6.2	—	—	—	—	—	—
BT5-1	4.5-6.0	—	—	—	—	—	2-3% Sn
OT4-1	1.0-2.5	0.7-2	—	—	—	—	—
OT4	3.5-5.0	0.8-2	—	—	—	—	—
BT4	4.5-6.0	0.8-2	—	—	—	0.18	0.5-1.5 Nb, 10-12 Zr
BT18	7.2-8.2	—	—	0.2-1.0	—	0.5	—
				α+β-alloys			
BT6	5.5-7.0	—	4.2-6.0	—	—	—	—
BT8	6.0-7.3	—	—	2.8-3.8	—	0.2-0.4	—
BT14	4.5-6.3	—	0.9-1.9	2.5-3.8	—	—	—
				β-alloys			
BT3-1	5.5-7.0	—	—	2.0-3.0	1.0-2.5	0.15-0.4	0.2-0.7 Fe
BT22	4.0-5.7	—	4-5.5	4-5.5	0.2-2	—	0.5-1.5 Fe
BT15	2.3-3.6	—	—	6.8-8.0	9.5-11.0	—	—

[1] That is, retain β-phase at all temperatures.

[2] Vanadium, molybdenum, niobium, tin, iron, chromium, and manganese.

Table 21.3. Mechanical Properties of Commercial Titanium Alloys

Alloy Grade	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %	ψ, %	a_{n_I}, kgf m/cm²
		α-alloys			
BT4	80-90	70-80	15-22	20-30	—
T4	70-85	55-65	15-40	25-55	3.5-6.5
		α+β-alloys			
BT6	90-100	80-90	8-13	30-45	4-8
BT8	105-118	95-110	9-15	30-55	3-6

5% Al. Without a third alloying element, this would be an α-alloy (such as Grade BT5). An additional alloying of Ti + 5% Al alloys with β-stabilizers[1] produces a two-phase α + β structure. Despite large differences in alloying, all α + β alloys with 5% Al have quite similar mechanical properties: $\sigma_t \approx$ $\approx$ 100 kgf/mm², $\delta \approx 15$ per cent, $\psi \approx 30$ per cent, and $a_{n_I} = 5$ kgf m/cm². A higher ductility but a lower strength is exhibited by an alloy with a lower aluminium content (OT4) and also by α-alloys (BT5 and BT1).

21.5. HEAT TREATMENT OF TITANIUM ALLOYS

Recrystallization annealing of titanium and its alloys is carried out at 700-800°C, i.e. well above the recrystallization temperature (500°C). Such a high temperature level can quickly eliminate the strain-hardening effect. Owing to the phase transformations discussed earlier, titanium alloys can be subjected to various procedures of hardening and tempering (age-hardening), though the changes caused in them by heat treatment are not as substantial as with heat treatment of steels.

The most important type of heat treatment of titanium is that which can refine the grain by phase recrystallization and thus improve the plastic properties.

Since however, the structure of alloys can be varied in a wide range, as follows from the diagrams of isothermal transformation of β-phase (see Fig. 21.6), the properties of the alloys can also be changed appreciably.

The mechanical properties of an as-hardened alloy are determined by the content of β-, α′- and α″-phase in it, the strengthening effect being mainly due to α″-phase (a distorted α′-phase, also of martensitic origin). The concentration of α″-phase depends on the temperature of heating for hardening, cooling rate, and the content of alloying β-stabilizers. As-hardened alloys are not, however, much strengthened compared to their annealed state.

The main strengthening effect is obtained by the tempering (age-hardening) of as-hardened alloys or by isothermal heat treatment.

[1] Molybdenum, silicon, manganese, niobium, zirconium.

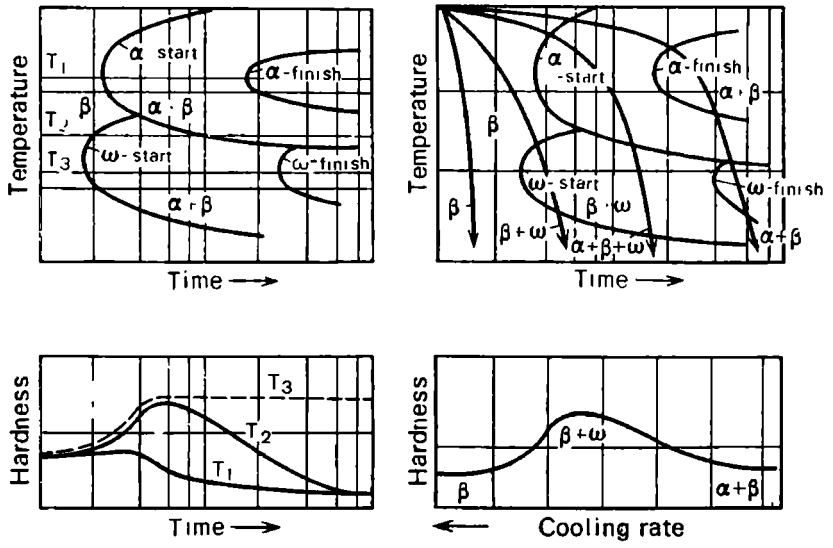

Fig. 21.7. Effect of the temperature of isothermal decomposition and cooling rate on the hardness and structure of titanium alloys (schematic)

Figure 21.7 shows the variations in the properties (hardness) of a titanium alloy which has a β- or α + β structure on heating to a high temperature.

Hardening (the formation of α + β + α′ + α″ structure) gives a hardness slightly less than 250 *HB*. A lower hardness is obtained if the isothermal transformation is carried out in the upper subcritical temperature region (T_1) which causes only the β → α transformation, rather than the β → α′ or β → α″ transformation.

The transformation at T_2 will form ω-phase (β → ω) and increase the hardness of the alloy; a subsequent transformation of ω-phase (ω → α) will produce an equilibrium (β + α) structure in the alloy.

In view of the foregoing, the properties of an alloy will vary depending on the rate of cooling (Fig. 21.7). No strengthening effect can be obtained by severe quenching which fixes the β-state or by slow cooling (annealing) which creates the α-state, whereas cooling at an intermediate rate can increase the strength due to the formation of ω-phase.

It should be noted that the high-strength phases (α″ and especially ω) formed by heat treatment can lower substantially the ductility and toughness, because of which this method is not effective for increasing the structural strength of titanium alloys.

Titanium alloys have very poor antifriction properties and are unsuitable for making friction elements. The wear resistance of titanium alloys can be improved by chemical heat treatment: by carburizing or better by nitriding. Nitriding is carried out at 850-950°C for 15-25 h in dissociated ammonia or in dry oxygen-free nitrogen. As a result of nitriding, a thin (around 0.1 mm) nitrogen-saturated layer is formed, having a hardness of 1 000-1 200 *HV*.

21.6. IMPURITIES IN TITANIUM ALLOYS

Titanium is a chemically active element. It is difficult to make titanium of a high purity and also difficult to protect it from an adverse influence of the surroundings. It is therefore essential to

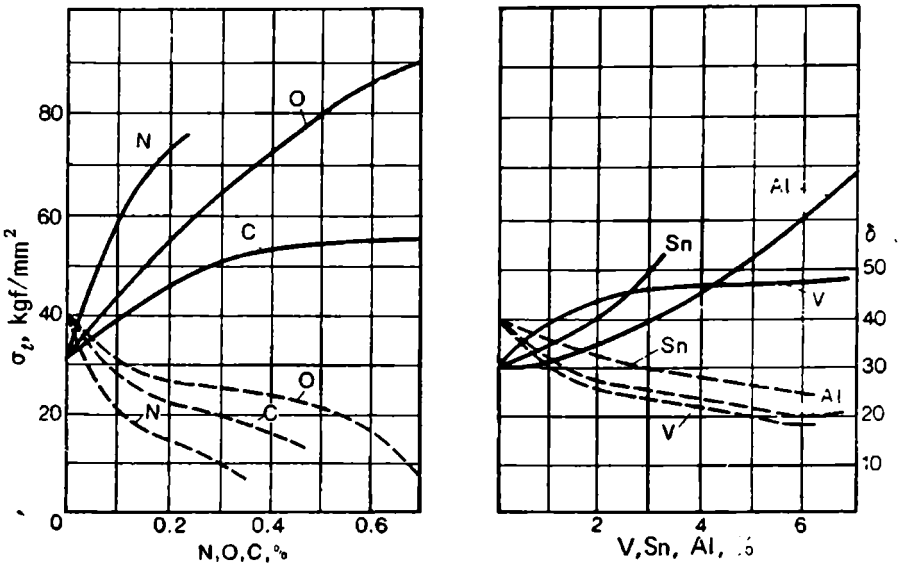

Fig. 21.8. Effect of various elements on the mechanical properties of titanium. Solid line — ultimate strength; dotted line — elongation

have a pure original titanium and to avoid its saturation with various elements in the technological procedures.

When being heated, titanium can absorb oxygen, nitrogen, hydrogen and carbon which form interstitial solid solutions with Ti_α and Ti_β, as distinct from common alloying elements (vanadium, aluminium, tin, etc.) which form substitutional solid solutions.

Interstitial solid solutions can increase σ_t more appreciably[1] than substitutional solid solutions, but they lower the ductility (Fig. 21.8). The effect of interstitial impurities on the properties of titanium alloys is roughly 10 times that produced by substitutional impurities.

Alloying with elements forming substitutional solid solutions can produce a better combination of toughness and ductility than is possible on alloying with interstitial elements. For that reason, interstitial elements are considered harmful impurities and their content in titanium alloys is limited.

The allowable contents of interstitial elements are different for various grades of titanium sponge depending on purity (0.04-0.10% O, 0.02-0.06% N, 0.03-0.06% C). The toughness properties of titanium alloys are influenced especially strongly by hydrogen. At a hydrogen content of 0.02-0.05 per cent, the impact toughness can drop down to zero, because of which the hydrogen content in titanium alloys is limited to 0.01 per cent (more strictly, from 0.005 to 0.015 per cent in various alloy grades).

Silicon and iron are also harmful impurities in most titanium alloys, but their effect is less profound than that of interstitial impurities (since iron and

[1] Owing to large distortions of the crystal lattice.

silicon form substitutional • solid solutions with titanium). Depending on the grade, titanium alloys should contain not more than 0.07-0.3 per cent iron and 0.04-0.10 per cent silicon.

21.7. CORROSION RESISTANCE OF TITANIUM

Apart from having a high strength-to-density ratio (owing to which titanium alloys are widely used in special branches of engineering, such as aircraft and rocket engineering, etc.), titanium also possesses a high corrosion resistance in most aggressive media and excels stainless steels in that respect.

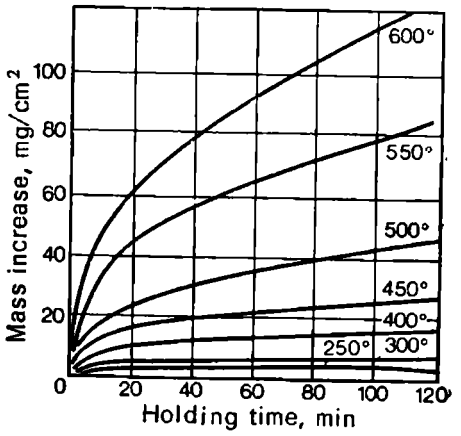

Fig. 21.9. Oxidation of titanium at various temperatures (I.I. Sidorin)

The high corrosion resistance of titanium is due to a dense protective oxide film (TiO_2) which forms on its surface. If the film is insoluble in a given surrounding medium, the metal can be regarded to be absolutely stable in that medium. For instance, sea water can dissolve titanium to a depth equal to the thickness of a paper sheet in 4 000 years. If a medium can dissolve the titanium oxide film, the application of the metal in it is inadmissible.

It is more easy to enumerate the media in which titanium is unstable: these are hydrofluoric, hydrochloric, sulphuric and orthophosphoric acids among inorganic acids and oxalic and acetic acids among organic ones.

When being heated, titanium can absorb gases (oxygen, nitrogen, hydrogen) from the atmosphere, the process being more intensive at a higher temperature (see Fig. 21.9). For that reason the saturation of titanium with gases, in the first place with oxygen, during process or operational heating should be prevented by using controlled atmospheres.

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Chapter 22

HIGH-MELTING METALS

22.1. GENERAL

All the metals whose melting point is above that of iron (1 539°C) are regarded as high-melting metals (except for platinum and uranium group metals and some rare-earth metals).

Therefore, the following metals should be related to the high-melting group: vanadium ($t_{m.p.}$ = 1 900°C), tungsten (3 410°C), hafnium (1 975°C), molybdenum (2 610°C), niobium (2 415°C), rhenium (3 180°C), tantalum (2 996°C), technetium (2 700°C), titanium (1 672°C), chromium (1 875°C), and zirconium (1 855°C). All these elements occupy a definite place in the Periodic Table and relate to transition group metals (see Table 1.2).

Consider briefly the properties and structural peculiarities of high-melting metals, except for titanium[1] and technetium[2].

High-melting metals have attracted great attention. The point is that the working temperatures in missiles, high-speed aircraft and space ships and in some elements or units of various machines attain 1 500-2 000°C, i.e. are close to, or even higher than, the melting point of iron, cobalt or nickel—the base metals of all common heat-resisting alloys. Only high-melting metals can be used reliably for these purposes.

Though pure high-melting metals possess a higher heat resistance compared to other metals, they can be made more heat-resisting by alloying. For that reason, alloys based on molybdenum, tungsten, tantalum or niobium are used instead of pure metals in high-melting applications.

It should be also noted that high-melting metals have an exceptionally high resistance to acids (see Fig. 19.2), which makes their use in chemical engineering very promising. The principal physical properties of high-melting metals are given in Table 22.1.

Apart from having high melting and boiling points and, respectively, high temperatures of recrystallization (which is given

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[1] It differs substantially in the properties and behaviour from the other high-melting metals.

[2] Technetium is available only in very small quantities, even not sufficient for a detailed laboratory analysis of its properties.

Table 22.1. Physical Properties of High-melting Metals

Metal	Recrystallization point, °C	Melting point, °C	Boiling point, °C	Crystal lattice structure	Density, g/cm³	Heat conductivity, cal/cm deg s	Linear expansion (at 20°C), 10^{-6} deg
Tungsten	1 500	3 410	6 700	C8	19.3	0.48	4.5
Rhenium	1 800	3 170	5 630	H12	21.0	0.17	6.7
Tantalum	1 000	2 996	6 100	C8	16.6	0.13	6.6
Molybdenum	1 000	2 625	4 800	C8	10.2	0.35	5.4
Niobium	1 100	2 415	3 300	C8	8.56	0.12	7.1
Hafnium	—	1 975	5 400	H12 and C8	13.36	0.053	6.0
Vanadium	—	1 900	3 350	C8	6.11	0.074	9.7
Chromium	800	1 890	2 469	C8	7.2	0.16	6.2
Zirconium	—	1 855	3 577	H12 and C8	6.0	0.04	5.8

approximately for commercial-purity metals), these metals have the same type of crystal lattice—body centred cubic (except for rhenium and hafnium), have no polymorphic modifications[1], possess a high (higher than that of iron) density (except for vanadium and chromium) and a low coefficient of thermal expansion (except for vanadium).

The high melting points of these metals are due to the high forces of interatomic bond. All the metals mentioned are relatively rare and therefore expensive.

High-melting metals are produced in the form of a compact mass by the methods of powder metallurgy[2] and electric-arc melting[3].

As has been noted, most high-melting metals have (like α-iron) a body-centred cubic lattice and a typical feature of being embrittled at definite temperatures. The temperature of transition to the brittle state depends on the nature and purity of a metal.

As may be seen from Fig. 22.1, a plastic metal (i.e. capable of contracting substantially in the cross-section) becomes brittle below a definite temperature. For tungsten and chromium, this transition point is above room temperature, for molybdenum, at the level of

[1] Except for hafnium which undergoes an allotropic $\alpha \rightleftarrows \beta$ transformation at 1 310°C and for zirconium which undergoes an allotropic $\alpha \rightleftarrows \beta$ transformation at 862°C.

[2] That is, a metallic powder is sintered and then pressed or rolled to the desired shape.

[3] The process is carried out in vacuum, with the molten metal serving as one of the electrodes.

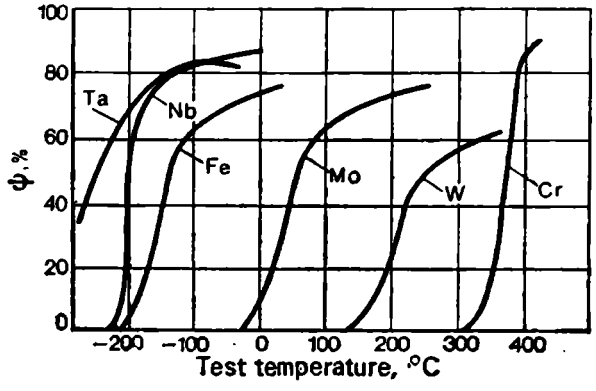

Fig. 22.1. Serial curves of the relative contraction of high-melting metals in recrystallized state

room temperature, and for niobium (as for iron), below room temperature.

Among all the high-melting metals, niobium, tantalum, molybdenum and tungsten (often called 'the big four') have the widest practical application.

22.2. INTERACTIONS OF HIGH-MELTING METALS WITH OTHER ELEMENTS. COMMERCIAL ALLOYS

The metals of the big four can form with other high-melting metals and with each other either solid solutions in any concentrations or solid solution of a wide homogeneity.

The metallic elements which stand far from the high-melting metals in the Periodic Table are only slightly soluble in the latter and have a tendency to form intermetallides (tungstenides, molybdenides, etc.).

An especially strong effect is produced by non-metallic elements having a small atomic radius: they can form interstitial solid solutions with molybdenum, tungsten, niobium, tantalum, etc., and in addition, their solubility is substantially temperature-depending. This results in the precipitation of corresponding disperse phases (oxides, carbides, etc.) approximately in a temperature range of 1 800-1 200°C and strong embrittlement of alloys. In order to avoid embrittlement, the metal should be purified from these elements to lower their content below the solubility limit. The latter can be taken as the solubility at 1 200°C (Table 22.2).

As may be seen from the table, the solubility of interstitial impurities in the metals of group VA is two or three orders of magnitude greater than that in the metals of group VIA.

Since all interstitial elements affect similarly the properties of high-melting alloys (impair the ductility by raising the ductile-to-brittle transition point), it is essential for obtaining a plastic metal that the sum C + N + O in chromium, molybdenum or tungsten

Table 22.2. Solubility of Interstitial Elements in High-melting Metals at 1 200°C, % by mass (approximate values)

Group of metals	Hydrogen	Carbon	Nitrogen	Oxygen
VIA (Cr, Mo, W)	10^{-4}-10^{-5}	10^{-3}-10^{-4}	10^{-3}-10^{-5}	10^{-2}-10^{-3}
VA (V, Nb, Ta)	10^{-1}-10^{-2}	10^{-1}-10^{-2}	1-10^{-1}	1-10^{-1}

Table 22.3. Compositions of Most Common High-melting Alloys

Base	Alloy Grade	Alloying elements, %	Manufacturing country
Nb	FS-80	1 Zr	USA
	D-31	10 Mo, 1 Ti, 0.1 C	
	B-66	5 Mo, 5 V, 1 Zr	
	D-43	10 W, 1 Zr, 0.1 C	
	F-48	15 W, 5 Mo, 1 Zr, 0.1 C	
	WO-103	10 Hf, 1 Ti, 0.7 C	
	BH-2	4.5 Mo, <0.05 C	USSR
	BH-2A	4 Mo, 0.7 Zr, <0.08 C	
	BH-4	10 Mo, 1.5 Zr, 0.3 C	
Mo	TM	0.5 Ti, 0.02-0.05 C	USA
	TZM	0.5 Ti, 0.08 Zr, 0.015 C	
	TZC	1.25 Ti, 0.3 Zr, 0.15 C	
	WZM	25 W, 0.1 Zr, 0.03 C	
	ЦМ-2А	0.1 Zr, 0.1 Ti, <0.004 C	USSR
	ЦМ-6	0.15 Zr, 0.002 B	
	ЦМ-3	0.3 Zr, 0.02 C	
	ВМ-1	0.15 Zr, up to 0.4 Ti, <0.01 C	
	ВМ-2	0.35 Zr, up to 0.2 Ti, <0.02 C	
	ВМ-3	0.45 Zr, 1 Ti, 1.4 Nb, 0.35 C	
Ta	F-60	10 W	USA
	Nb6-7.5 V	30 Nb, 7.5 V	
W	—	1-2 ThO_2	USA
	—	15 Mo	

be not more than 0.001 per cent*; this is an extremely difficult practical problem which has no satisfactory solution as yet. For vanadium, niobium and tantalum, the sum C + N + O may be of an order of 0.1 per cent (more probably, 0.05%), which is attainable practically. This is why commercial chromium, molybdenum and tungsten (and their alloys) are brittle (their ductile-to-brittle transition point is above room temperature), while vanadium, niobium and tantalum are plastic (with the ductile-to-brittle transition point being below room temperature), see Fig. 22.1.

As has been noted earlier, pure high-melting metals are used less frequently than their alloys.

Analysis of the interaction of various elements with high-melting metals and direct studies into the effect of various elements (E.M. Savitsky, N.N. Morgunova) suggest the following general recommendations:

(1) high-melting metals can be alloyed in an amount of a few per cent only with high-melting metals; the metals of group VA (vanadium, niobium, tantalum) can be alloyed more heavily than those of group VIA (chromium, molybdenum and tungsten);

(2) oxygen is a more harmful element than carbon, so that the latter is added in small amounts (up to 0.05-0.1%) for deoxidation and 'rigid' alloying.

Table 22.3 gives the compositions of selected high-melting alloys produced in the USSR and USA; these alloys are employed along with commercially pure high-melting metals. Note that only commercially pure tantalum is used in the USSR while its alloys have no application.

22.3. MECHANICAL PROPERTIES AND HEAT RESISTANCE

The properties of high-melting metals at high temperatures are of the greatest practical importance. To characterize these metals as structural materials, it is also essential, however, to know how their mechanical properties vary over a wide range of working temperatures. The typical temperature curves of the ultimate tensile strength and ductility characteristics of various high-melting metals in recrystallized state are shown in Fig. 22.2. As might be expected, the metals having a higher melting point have a higher strength at higher temperatures.

That the strength of a metal is a function of its melting point can be verified by comparing the strength values of various metals at their homologous temperatures ($T_{test}/T_{m.p.}$ = constant). The relation between the homologous temperature and ultimate tensile strength for molybdenum and niobium (nickel is taken for comparison) shows that there are three temperature intervals which differ from one another in the effect of temperature on strength (see Fig. 22.3).

In a temperature range above $0.6T_{m.p.}$, the ultimate tensile strength is determined by the nature and magnitude of the energy

* It is possible to sum up weight percentages, since the atomic weights of carbon, nitrogen and oxygen are very close to one another.

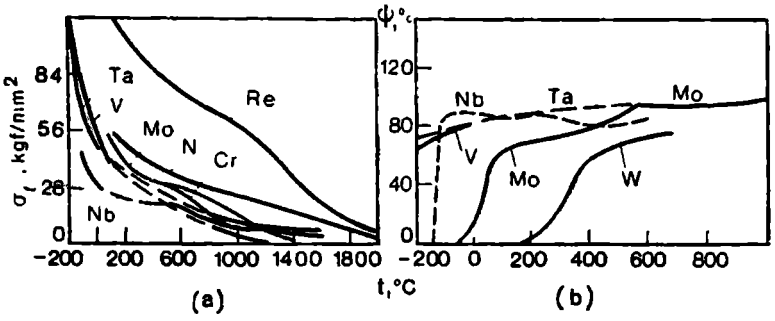

Fig. 22.2. Temperature curves of the ultimate tensile strength (*a*) and relative contraction (*b*) of high-melting metals

of interatomic bond in the metal, and the strength of all the metals is equal at equal homologous temperatures.

In the temperature range from 0.2 to $0.6T_{m.p.}$, the strength is determined mainly by the structure (grain size, the presence of a second disperse phase, strain hardening, etc.) and is quite different in various metals. In this temperature interval, the properties of metals depend only slightly on temperature.

In the low-temperature range (less than $0.2\text{-}0.3T_{m.p.}$) the strength is heavily dependent on temperature. The most essential feature in the behaviour of the metals in this temperature range is an intensive loss of ductility associated with the passage through the ductile-to-brittle transition point. Cold brittleness of high-melting metals will be discussed in the next section. Let us analyse here the mechanical properties in the intermediate temperature range from 0.2 to $0.6T_{m.p.}$ since, on the one hand, this is the range of working temperatures and, on the other, the mechanical properties are structure-sensitive.

Interstitial impurities increase the strength characteristics in the range of 0.2 to $0.6T_{m.p.}$. This has been noted mainly for niobium and tantalum which is associated with a high solubility of oxygen, nitrogen and carbon in these metals.

In molybdenum and tungsten, the effect of these impurities in the solid solution is almost unnoticeable owing to their poor solubility.

Deformation and recrystallization. High-melting metal semiproducts usually have a deformed fibrous structure (Fig. 22.4),

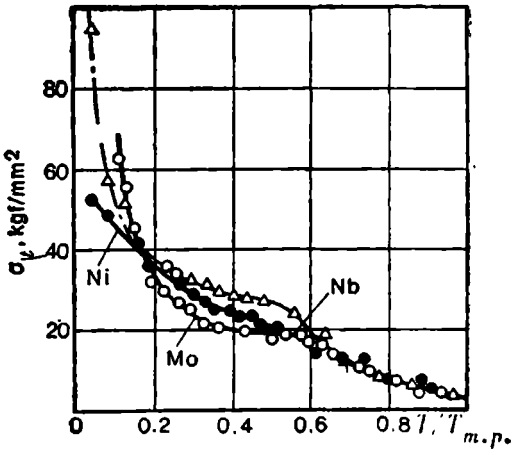

Fig. 22.3. Strength *versus* homologous temperature ($T/T_{m.p.}$) curves for molybdenum, niobium and nickel

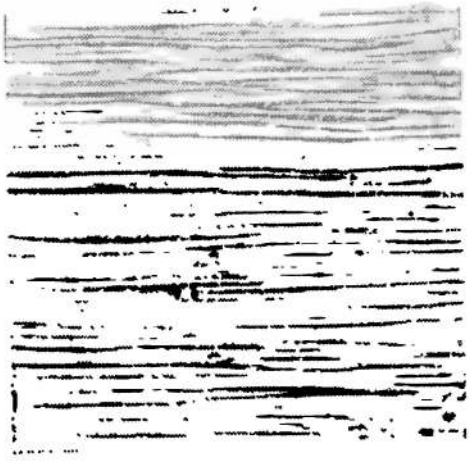

Fig. 22.4. Microstructure of deformed molybdenum

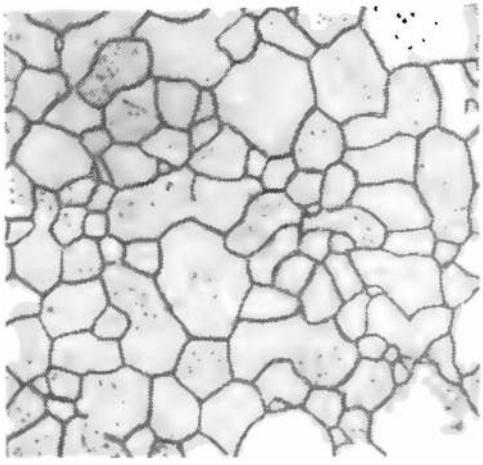

Fig. 22.5. Microstructure of recrystallized molybdenum

which is associated with the fact that the deformation of high-melting metals, at the final stages of making sheets, rods, strips, etc., is usually carried out at room temperature or with a slight preheating, i.e. always below the recrystallization point. In recrystallized state, all high-melting metals usually have a polyhedral structure (Fig. 22.5). In deformed structures, fibres are oriented along the direction of rolling. Comparing the plastic niobium (or tantalum) in as-deformed and as-recrystallized states can only confirm the well known relationship that a deformed (strain-hardened) metal has a higher strength and lower ductility than in as-recrystallized state (Table 22.4).

The ductile-to-brittle transition point of deformed molybdenum (or tungsten) lies lower than that of the recrystallized metal (to be discussed later in more detail), because of which the ductility of as-deformed molybdenum is higher than in as-recrystallized state (see Table 22.4).

Table 22.4. Mechanical Properties of Deformed and Recrystallized Niobium and Molybdenum

Metal	State	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %	ψ, %
Niobium	Deformed	75	60	20	30
	Recrystallized	52	47	27	37
Molybdenum	Deformed	75	67	30	40
	Recrystallized	55	55	1	2

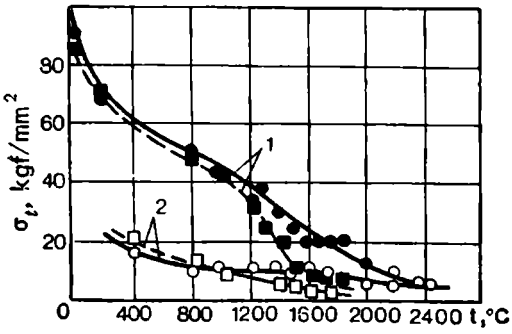

Fig. 22.6. Effect of temperature on the ultimate strength of Mo + 0.12% Zr alloy (*1*) as deformed; (*2*) recrystallized

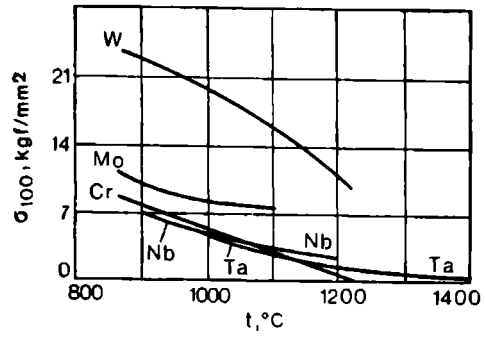

Fig. 22.7. Effect of temperature on the long-term strength (100-h) of various high-melting metals

All high-melting metals, including molybdenum and niobium, are extremely plastic when being tested above the ductile-to-brittle transition point—$\psi = 100$ per cent (see Fig. 3.9).

The mechanical characteristics of high-melting metals (as of all other metals and alloys) depend on the degree of cold plastic deformation.

The effect of strain hardening on the mechanical characteristics diminishes as the test temperature increases. For instance, molybdenum alloy Grade ЦМ-2А has the same values of strength and ductility in as-deformed and as-recrystallized states at temperatures of 1 800-2 000°C (Fig. 22.6).

High-melting metals are alloyed with other elements to increas their heat resistance.

Figure 22.7 shows the effect of temperature on the long-term strength (100-h) for pure metals of the groups V and VI.

As may be seen, the heat resistance of pure metals is relatively low. This is why alloys of high-melting metals, but not pure metals, are usually employed as structural heat-resisting materials.

Alloying of high-melting metals is controlled by the general rules according to which the strengthening effect is obtained by the formation of fine-disperse precipitates with distances of an order of 100 Å between particles, and also by elements dissolved in the solid solution.

Niobium and tantalum alloys can be strengthened appreciably by alloying their solid solution. As regards molybdenum and tungsten, their heat resistance cannot be improved essentially by this method, since most elements are poorly soluble in them. Their heat-resisting properties are commonly improved by precipitation hardening.

Niobium and tantalum are usually alloyed heavily with molybdenum, titanium, tungsten and other, preferably high-melting, metals. Molybdenum is alloyed with tungsten and, in small quantities, with titanium and zirconium which are stronger carbide-formers than molybdenum (or tungsten) and can form a secondary

carbide phase very low in carbon (a few hundredths of a per cent). This phase produces a strong hardening effect upon precipitation.

Heat-resisting properties of selected high-melting alloys are given in Tables 22.5 through 22.7.

Table 22.5. Heat-resisting Properties of Niobium and Molybdenum Alloys

Alloy Grade	Composition, %	σ_t, kgf/mm²			σ_{100}, kgf/mm²			
		1 100°C	1 200°C	1 300°C	1 100°C	1 200°C	1 300°C	1 315°C
		Niobium-base alloys						
Niobium	Commercially pure	7.5	6.5	4.2	3.2	2.8	—	—
BH-2	4.5 Mo, < 0.05 C	31-35	18-20	—	14	—	—	—
BH-4	10 Mo, 1.5 Zr, 0.3 C	70	55	—	28	—	10	—
BH-2A	4 Mo, 0.7 Zr, < 0.08 C	45	30	—	13	—	—	—
		Molybdenum-base alloys						
Molybdenum	Commercially pure	19	—	—	8	—	—	—
ЦМ-2А (ВМ-1)	0.1 Zr, 0.1 Ti, 0.004 C	38	34	—	23	8	—	—
ВМ-2	0.35 Zr, 0.2 Ti, 0.02 C	48	45	—	26	15	—	—
ВМ-3	0.45 Zr, 1 Ti, 1.4 Nb, 0.35 C	—	—	50-57	—	—	—	25
ЦМ-3	0.3 Zr, 0.02 C	55	50	40	—	18	—	—

Table 22.6. Heat-resisting Properties of Tungsten-base Alloys

Alloy Grade	Composition, %	σ_t, kgf/mm², at			σ_{100}, kgf/mm², at 1 650°C
		1 650°C	1 927°C	2 204°C	
Tungsten	Commercially pure	17.5	11.4	4.4	3.2
W-Mo	15 Mo	25.3	7.9	3.9	5.1

Table 22.7. Heat-resisting Properties of Tantalum-base Alloys

Alloy Grade	Composition, %	σ_t, kgf/mm², at			σ_{100}, kgf/mm², at	
		1 315°C	1 650°C	1 927°C	1 315°C	1 650°C
Tantalum	Commercially pure	6.0	2.5	—	1.8	—
ES-60	10 W	27.8	13.5	6.0	16.2	6.0
WS-222	10 W, 2.4 Hf, 0.01 C	37.8	16.8	10.0	19.7	3.4

Since the heat resistance of various high-melting alloys can be almost the same in a particular temperature interval, other characteristics are often used as guiding ones for the selection of alloys for operation at high temperatures. Tungsten is the most brittle and most hard-to-produce among high-melting metals, so that tungsten-base alloys are only employed for working temperatures above 2 000°C and for the conditions of strong erosion wear. Tantalum-base alloys are the most expensive, because of which niobium- or molybdenum-base alloys are preferably used in a temperature interval of 1 000-1 500°C. Molybdenum alloys have the highest heat resistance; they are employed at temperatures above 1 200°C, sometimes up to 2 000°C. The selection of molybdenum and niobium alloys is determined by the requirements to ductility, weldability, corrosion resistance, etc.[1]

22.4. COLD BRITTLENESS OF HIGH-MELTING METALS

Though high-melting metals and their alloys are intended for operation at high temperatures, their cold brittleness, i.e. the position of their ductile-to-brittle transition point, is of great importance for the technology and operation.

In impact tests above the ductile-to-brittle transition point, a specimen of metal does not break, but bends between the supports of the machine. If recrystallized metal is impact-tested at lower temperatures, there occurs a change from no fracture to brittle fracture, i.e. the work of impact drops to zero (Fig. 22.8) and there appears a fracture that may be characterized as brittle[2] (Fig. 22.9).

[1] Niobium alloys have better technological properties but are inferior to molybdenum alloys as regards the heat resistance and stability in special media.

[2] It is interesting that molybdenum cannot be fractured by the brittle mechanism. Above the ductile-to-brittle transition point it only 'bends, but does not break' and in tension the cross-section of a specimen narrows to a point (see Fig. 3.9) and forms no fracture surface. Fracture surfaces can only form as a result of brittle fracture.

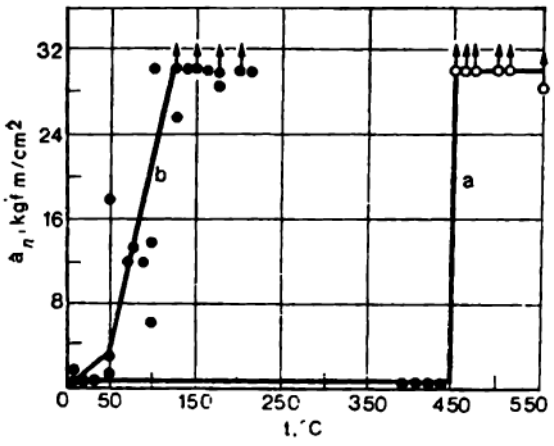

Fig. 22.8. Serial curves of the impact toughness of molybdenum
(*a*) recrystallized; (*b*) deformed

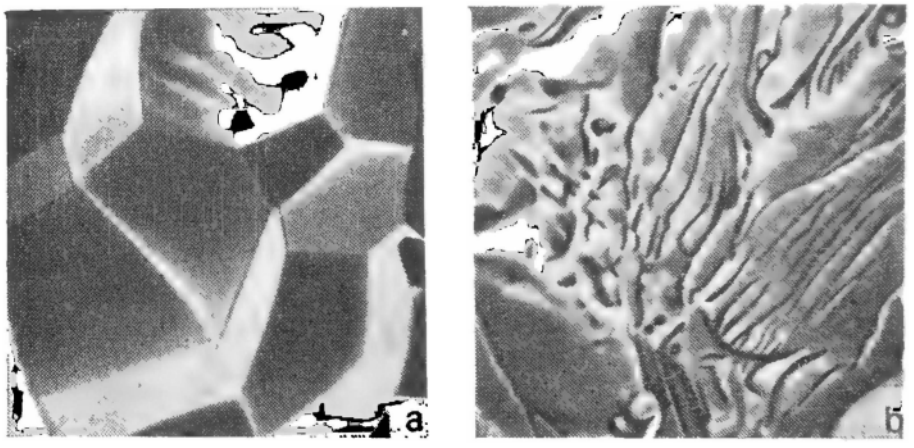

Fig. 22.9. Stereofractography of fracture in molybdenum
(*a*) intercrystalline fracture. ×30; (*b*) transcrystalline fracture, ×140

With a deformed-metal specimen, the passage to the brittle state occurs within a certain temperature interval, so that the specimen first breaks partially by the brittle mechanism and then bends without fracture. At lower temperature, the brittle fracture extends over a greater portion of the cross-section and in the limit (100-% brittle fracture) the specimen breaks into two halves.

It is important to note that the ductile-to-brittle transition point of deformed molybdenum is appreciably lower than in as-recrystallized state. At room temperature, deformed molybdenum is still embrittled not fully. In that connection, molybdenum is preferably used in strain-hardened state.

The ductile-to-brittle transition point can be affected substantially by alloying. Interstitial impurities can sharply shift this point towards higher temperatures.

For a given purity, b.c.c. metals differ appreciably from one another as regards their ductile-to-brittle transition point (see Fig. 22.1); the metals of group VI have a noticeably higher ductile-to-brittle transition point than those belonging to group V of the Periodic Table[1].

The difference between these two groups can be explained by the different solubility of hydrogen, carbon, nitrogen and oxygen in these metals (see Table 22.2).

In commercial purity niobium and tantalum, interstitial impurities, when contained at the common level, are present in the solution. In molybdenum and tungsten, they are poorly soluble and are present as disperse inclusions (carbides, nitrides, oxides) on the grain boundaries or in the boundary volumes. This fact promotes brittle fracture and for that reason molybdenum and tungsten have an appreciably higher ductile-to-brittle transition point than the former metals.

Purification from interstitial impurities can lower the ductile-to-brittle transition point and is one of the possible means for improving the ductility of high-melting metals. A deep purification from interstitials is still a complicated technological problem.

Substitutional metallic elements when dissolved in molybdenum or other high-melting metals, in the general case impair the ductility and raise the ductile-to-brittle transition point. Small additions of substitutional elements can serve as deoxidizers and lower the ductile-to-brittle transition point. This effect, in particular, can be produced by aluminium, cerium, titanium or zirconium in a concentration of 0.1-0.5 per cent. A heavier alloying with substitutional elements always raises the ductile-to-brittle transition point. An exception is rhenium which lowers the ductile-to-brittle transition point in molybdenum, tungsten and chromium (Fig. 22.10) owing to what is called the *rhenium effect*, though a noticeable positive effect of rhenium alloying in group VI metals can only be obtained by adding this element in a large concentration (30-50%). Since rhenium is very expensive (its cost is 1.5 times that of gold),

[1] Tantalum shows no appreciable drop in ductility on cooling down to —196°C.

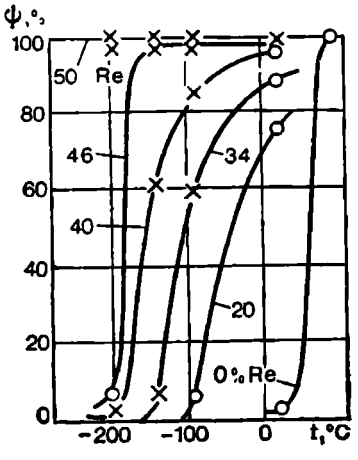

Fig. 22.10. Temperature variation of plasticity of molybdenum with different rhenium content

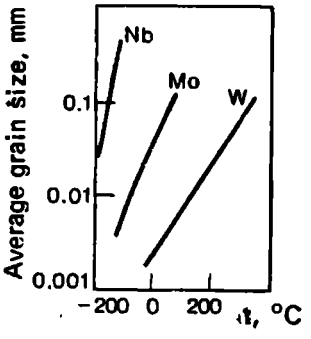

Fig. 22.11. Effect of grain size on the ductile-to-brittle transition point of high-melting metals

the method has found no application for improving chromium, molybdenum and tungsten alloys.

The nature of the rhenium effect is still being studied and disputed.

The position of the ductile-to-brittle transition point can be affected appreciably by the structure of the metal, and therefore, by the conditions of deformation and heat treatment.

Since brittle fracture is associated in the first place with the presence of interstitial impurities on the grain boundaries, the area of the grain boundaries, and therefore, the size of grain are of high importance. As may be seen from the curves in Fig. 22.11, the ductile-to-brittle transition point of niobium, molybdenum and tungsten lowers with grain refinement.

The ductile-to-brittle transition point of all high-melting metals in as-recrystallized state is usually appreciably higher than in as-deformed state. The difficulties in welding of molybdenum and tungsten are associated exactly with this circumstance: the recrystallized metal in the weld-affected zone becomes brittle, since its ductile-to-brittle transition point is higher than in as-deformed state in the main metal. Therefore, the problem of developing weldable high-melting alloys based on molybdenum or tungsten consists in lowering the ductile-to-brittle transition point of the alloys in as-cast and recrystallized state below the room temperature.

22.5. OXIDATION RESISTANCE AND OXIDATION PROTECTION

The principal disadvantage of most high-melting metals is their poor resistance to oxidation. An exception is chromium, but its heat resistance is lower than that of nickel-chrome alloys.

As has been found by studies into the scaling resistance of molybdenum, tungsten, niobium, tantalum and chromium, the rate of oxidation of molybdenum is six times that of tungsten, while the latter oxidizes three times quicker than niobium or tantalum (Fig. 22.12). The high oxidation rates of molybdenum and tungsten can be explained by the low melting points of their oxides MoO_3 and WO_3 (795 C for MoO_3), whereas Nb_2O_5 and Ta_2O_5 oxides are stable at the temperatures up to 1 370°C. Niobium and tantalum, however, have a higher solubility for oxygen, because of which their surface layers can be saturated appreciably with oxygen, which gives a noticeable change in their properties.

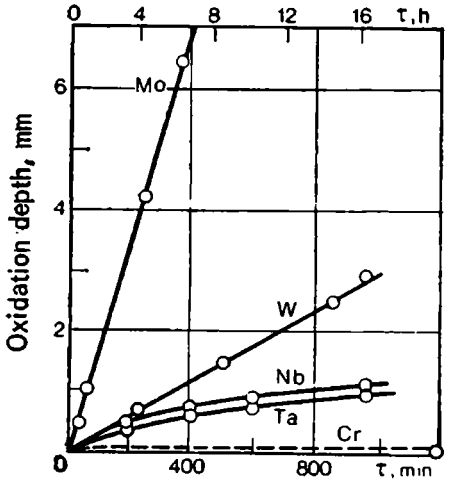

Fig. 22.12. Oxidation curves (at 1 039 C) for various high-meltingmetals (E.M. Savitsky)

Much research work has been done to develop heat-resisting alloys based on molybdenum and niobium. These attempts should however be regarded as unsuccessful, since heavy alloying is needed to improve noticeably the resistance to oxidation, which inevitably impairs the ductility and, as a rule, lowers the melting point and thus lowers the heat resistance. Further, though in some cases it is possible to diminish the oxidation rate of molybdenum by a factor of 100, the absolute values of heat resistance of molybdenum alloys remain much lower than in Fe-Ni alloys.

It follows from the comparison of the oxidation rates of these metals that niobium-base alloys can be partly applicable in oxidizing media, while molybdenum alloys are utterly unsuitable for the purpose.

Studies have been carried out for a long time to find appropriate protective coatings for high-melting metals. A number of metallic, intermetallic and ceramic coatings have been developed to prevent oxidation of high-melting metals.

Thermodiffusion silicide coatings ($MoSi_2$, WSi_2) are considered to be the best for molybdenum and tungsten. Nichrome coatings are also in use.

A silicide coating on tungsten can prevent the oxidation of the metal for 10 hours at 1 820°C.

The application of surface coatings is limited to elements to be used for a short time (usually perishable elements). Owing to differences in the linear expansion of the main metal and coating, the heating and cooling cycles can quickly cause detachment of the coating from the metal and the development of surface cracks and thus destroy the coating.

High-melting metals are used widely for operation at high temperatures in vacuum, hydrogen and inert gases, but not in oxidizing media.

22.6. CORROSION RESISTANCE

Despite their low resistance to oxidation (gaseous corrosion) at high temperatures, all high-melting metals are extremely acid-resisting.

In boiling sulphuric acid, one of the most aggressive media, acid-resisting Cr-Ni-Mo-Cu steel can operate at the H_2SO_4 concentrations up to 5 per cent, Hastelloys (80% Ni and 20% Mo) at the concentrations up to 20 per cent, and tantalum, at the concentrations up to 80 per cent (see Fig. 19.12).

Tantalum is the most acid-resisting among high-melting metals. Niobium has a higher acid resistance than iron and nickel alloys, but is inferior to tantalum.

The use of niobium instead of tantalum may be attractive because niobium is less expensive. The corrosion resistance of niobium alloys, with an appropriate alloying, can be made close to that of tantalum.

The corrosion resistance of niobium can be improved by the additions of molybdenum and tantalum. Since a heavy alloying with molybdenum[1] can lower the ductility, alloying of niobium with tantalum is more promising. The addition of tantalum to niobium sharply increases the stability of the alloy in hydrochloric, phosphoric and boiling sulphuric acids (Fig. 22.13). An alloy of niobium and 25 per cent tantalum excels pure niobium in the corrosion resistance and approaches tantalum.

Since titanium in the concentrations up to 10 per cent does not impair the corrosion resistance of niobium, it is advisable to employ a ternary alloy[2]: 65% Nb + 25% Ta + 10% Ti.

When being used in boiling inorganic acids, molybdenum and tungsten excel appreciably niobium and are only slightly inferior to tantalum.

[1] A heavy alloying with molybdenum is needed to improve substantially the corrosion resistance of niobium.

[2] Titanium is added to lower the cost and density of the alloy and improve the process properties.

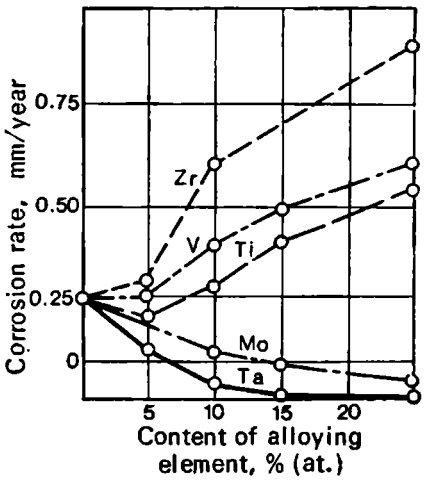

Fig. 22.13. Effect of alloying elements on the corrosion resistance of niobium in boiling 40-% sulphuric acid (the authors)

Since they are substantially less expensive than tantalum, they are very promising materials for chemical engineering. A wide application of molybdenum and tungsten is however limited by the difficulties in the manufacture of chemical machinery. It is possible to make chemical equipment from bimetallic (steel + molybdenum or coated molybdenum) sheets, rather than from pure molybdenum sheets. Bimetallic sheets are 2-3 times cheaper than pure molybdenum and have a higher ductility.

It should be remembered that the corrosion resistance of high-melting metals in strong acids is mainly determined by the composition of an alloy and depends only slightly on the structure and the process of manufacture.

High-melting alloys, in the first place tantalum, niobium-tantalum alloys and in some cases molybdenum, are the most acid-resisting among metallic materials. They can be used most effectively in media where all other materials are not sufficiently corrosion-resisting. These media include strong inorganic acids at elevated temperatures and some industrial media.

Despite the higher cost of high-melting materials compared to other corrosion-resisting materials, such as high-alloyed stainless steels or Hastelloys, the use of some high-melting alloys, such as Ta-Nb alloys, can be economically justified in some cases, since they have a higher corrosion resistance and therefore can serve for a longer time in chemical apparatuses.

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Chapter 23

ALLOYS WITH SPECIAL THERMAL AND ELASTIC PROPERTIES

23.1. LAWS OF THERMAL EXPANSION OF METALS AND ALLOYS. ALLOYS WITH SPECIFIED THERMAL EXPANSION

Instrument-making industry employs various alloys with certain specific properties, for instance, alloys with the linear expansion coefficient equal to that of glass, alloys having a zero coefficient of linear expansion or a very large coefficient, etc. Alloys to meet these requirements have a strictly definite composition and, like magnetic and electric alloys, are often called *precision alloys.*

Precision alloys (except for transformer iron) are made in very small quantities by the methods similar to alloy making in laboratories.

The relationship between the heating temperature and the expansion of a metal is usually curvilinear (Fig. 23.1).

The coefficient of linear expansion α increases with temperature: $\alpha_{t1} < \alpha_{t2}$ if $t_1 < t_2$.

The coefficients of linear expansion of selected metals at various temperatures are given in Table 23.1.

Table 23.1. Coefficients of Linear Expansion of Selected Metals

Metal	$\alpha \times 10^6$ at temperature, °C				
	0	100	200	600	800
Iron	11.3	12.2	12.7	14.5	14.8
Copper	16.7	17.0	17.4	18.8	19.6
Aluminium	22.8	23.7	24.5	27.9	—
Nickel	13.4	13.6	14.0	15.6	16.1
Cobalt	12.0	12.5	13.0	—	—
Platinum	8.9	9.1	9.2	9.7	9.9

Alloying elements can change the coefficient of linear expansion of the base metal; here two principal cases are possible: (a) if the two components form a mechanical mixture, the coefficient of linear expansion varies additively; (b) if the two components form a solid solution, the coefficient of linear expansion varies curvilinearly, but within the limits of the coefficients of the pure components.

There are however two anomalous systems, Fe-Ni and Fe-Pt, in which the variations of the linear expansion coefficient disobey the general laws. In iron-

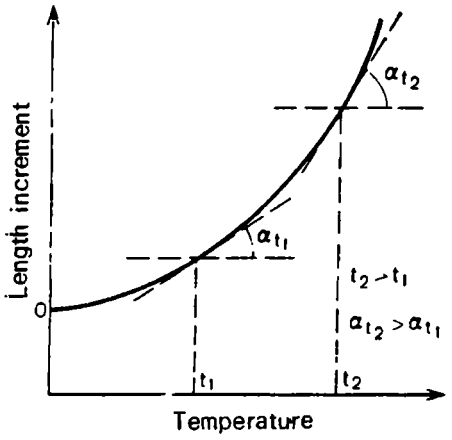

Fig. 23.1. Curve of expansion of an alloy with increasing temperature

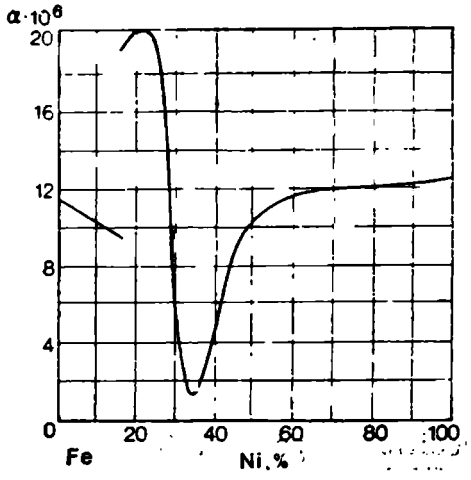

Fig. 23.2. Coefficient of linear expansion of Fe-Ni alloys

nickel alloys, the coefficient of linear expansion varies by a complex relationship[1] on addition of nickel (Fig. 23.2). As may be seen from the diagram, pure iron has the coefficient $\alpha = 11.6 \times 10^{-6}$. An alloy of Fe — 25% Ni has a coefficient of linear expansion almost twice as large ($\alpha = 20 \times 10^{-6}$). An alloy with 36% Ni, on the contrary, has a coefficient that is only one-eighth of that of pure iron ($\alpha = 1.5 \times 10^{-6}$).

An alloy of Fe + 36% Ni is called *Invar* and it does not practically vary linearly on being heated. The alloy is used in many instruments and elements whose dimensions should not vary with temperature. It should be remembered that Invar alloys retain the low coefficient of linear expansion only in the temperature interval from —80° to +100°C; beyond that interval their coefficient of linear expansion increases sharply.

An alloy of iron and 42% Ni can be characterized by a constant coefficient of linear expansion (about 7.5×10^{-6}) in the temperature interval from 20° to 200°C; beyond this temperature interval, its coefficient of linear expansion increases, i.e. the alloy expands more intensively (Fig. 23.3). In other words, Fe-Ni alloys have a temperature interval within which their coefficient of linear expansion remains constant. The upper temperature of this interval[2] is higher at a higher nickel content (Fig. 23.3).

Table 23.2 gives the compositions and the coefficients of linear expansion of selected Invar-type alloys.

Among the alloys given in Table 23.2, Grade H36 has found the widest application.

[1] The curve in Fig. 23.3 has a discontinuity corresponding to the change from α- to γ-solid solution.

[2] The temperature at which the coefficient of linear expansion of Fe-Ni alloy increases sharply coincides with the Curie point of that alloy.

Table 23.2. Composition and Thermal Properties of Invar Alloys

Alloy	Alloy Grade	Content of elements (approx.), %*		Thermal properties	
		Ni	Co	Coeff. of linear expansion, $\alpha \times 10^6$	Measured in temperature range, °C
Invar	H36	36	—	1.5	20-100
Superinvar	H31K6	30-34	4-6	1.0	20-60
Platynite	H48	48	—	9.0	20-300

* Balance iron.

Invar alloys exhibit a certain dimensional instability in time: a part made to specified dimensions may become smaller and then grow larger upon storage; these changes in dimensions are naturally very small in magnitude but can be of importance in elements whose dimensions should remain absolutely constant. The stabilization of linear dimensions is obtained by heat treatment which releases residual stresses, since the dimensional instability is due to the relaxation of the stresses formed during prior processing.

Replacement of a part of the nickel by cobalt gives what is called *Superinvar* alloy whose coefficient of linear expansion is still smaller than that of common Invar.

An alloy of iron, 29% Ni and 18% Co is called *Kovar*; its coefficient of linear expansion is $\alpha = 5 \times 10^{-6}$. The alloy is used for sealing molybdenum glass which has the same coefficient of linear expansion.

An alloy of Fe and 48% Ni has a coefficient of linear expansion of 9×10^{-6}, i.e. the same as that of glass and platinum (see Table 23.1). The alloy is called Platynite and is used in glass-to-metal seals.

23.2. ALLOYS WITH A CONSTANT ELASTIC MODULUS

In some applications, as in springs of precision instruments or in tuning forks, the metal must have a constant, i.e. temperature-independent, elastic moduli (E, G). In such cases recourse is made to *Elinvar* alloys which contain 36% Ni and 8% Cr, the balance being iron.

The temperature coefficient of the normal elastic modulus of these alloys varies within 18-23 $\times$ $\times 10^{-6}$ 1/°C, i.e. is only one-tenth that of carbon steel and only one-twentieth that of austenitic steel.

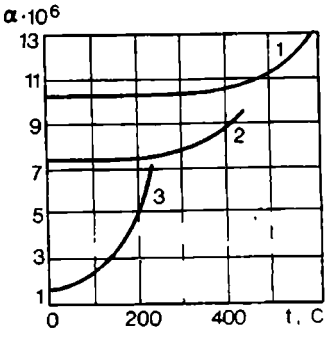

Fig. 23.3. Coefficient of linear expansion of Fe-Ni alloys at different temperatures. Nickel content, %
1 — 50; *2* — 42; *3* — 36

The compositions of commercial alloys with a low temperature coefficient of elastic modulus (of the Elinvar type and the like) are given in Table 23.3

Table 23.3. Composition (%) of Alloys Having a Low Temperature Coefficient of Elastic Modulus

Name	Alloy Grade	C	Cr	Ni	W	Other elements	Mn
Elinvar	ЭИ25	0.4	7.3-8.3	36.5-38.5	—	—	0.3-0.8
Elinvar	ЭИ574	0.7-0.8	7.0-8.9	33-35	2-4	—	2.0-3.0
	Н35ХМВ	1.14-1.26	8.5-9.5	34.3-35.7	2-4	1.8-2.2 Mo	0.8-0.9
Ni-Span-C	—	<0.06	5.1-5.7	41-43	—	2-2.6 Ti, 0.4-0.8 Al	0.3-0.6

The temperature coefficient of normal elastic modulus of the alloy Grade H35XMB is so small that, for instance, can ensure a clock rate accuracy of 0.5 s per day per °C.

Other properties of these alloys are on the average as follows:

	Elinvars	Ni-Span-C
Normal elastic modulus, kgf/mm²	16 000-17 000	18 000
Expansion, mm/(mm°C)	$7\text{-}8\times10^{-6}$	$7\text{-}8\times10^{-6}$
Electric resistivity, ohm mm²/m	0.9	0.9
Ultimate strength, kgf/mm² . . .	70-90	70-140
Elongation, %	15-20	40-70

Elinvar alloys are mainly used in as-strain-hardened state and Ni-Span-C, upon hardening and tempering or hardening and plastic deformation.

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Chapter 24

MAGNETIC STEELS AND ALLOYS

24.1. THE PRINCIPAL MAGNETIC CHARACTERISTICS OF METALS

Among all metals, only three (iron, cobalt, and nickel) exhibit ferromagnetism[1], i.e. can concentrate substantially the magnetic lines of force. The property is characterized by *magnetic permeability* which is tens or hundreds of thousands of units for ferromagnetic metals and is close to unity for other metals.

As is known, the substances whose magnetic permeability is greater than unity are called *paramagnetic* and those whose magnetic permeability is less than unity, *diamagnetic*.

The principal information on magnetic properties can be obtained by analysing magnetization curves, such as those shown in Fig. 24.1. Curve *2* in the figure is the primary or initial magnetization curve and curve *1* shows how the magnetic induction varies depending on the field strength in subsequent magnetization and demagnetization. The area confined between the two curves (which form what is called the *hysteresis loop*) determines the hysteresis losses, i.e. the energy spent for magnetization. Magnetization curves allow us to determine the following principal characteristics of magnetization.

Remanent induction B_r, i.e. the magnetic induction retained in a specimen upon magnetization and removal of the magnetic field (it is measured in gausses, Gs.).

Coercive force H_c is the field strength to be applied to a specimen for full demagnetization (it is measured in oersteds, Oe).

As follows from the form of the primary magnetization curve, the intensity of magnetization varies with the field strength. The intensity of magnetization is proportional to the tangent of the primary magnetization curve and is equal numerically to the ratio B/H.

The intensity of magnetization is called *magnetic permeability*; the magnetic permeability in very weak fields is called the *initial magnetic permeability*; the dimension of magnetic permeability is Gs/Oe.

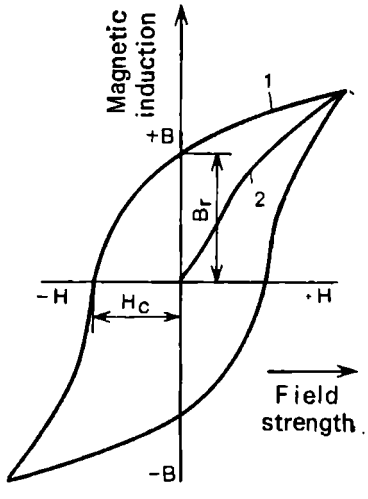

Fig. 24.1. Magnetization curve

1 — hysteresis curve; *2* — primary curve

Magnetic alloys are divided into two groups which differ greatly from each other in the form of hysteresis curve and the values of the principal magnetic characteristics. The first group includes magnetic-hard materials (Fig. 24.2*a*) which can

[1] Gadolinium, a rare-earth metal, is ferromagnetic at temperatures below 0°C.

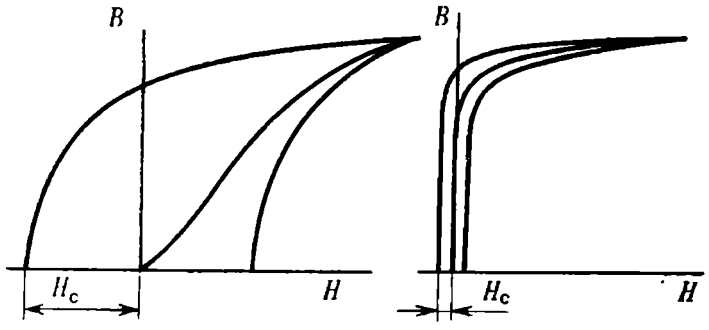

Fig. 24.2. Hysteresis curves of (*a*) magnetic-hard and (*b*) magnetic-soft alloys

be characterized mainly by a high value of H_c and are used in permanent magnets.

The second group comprises magnetic-soft alloys (Fig. 24.2*b*); they have a low value of H_c and low hysteresis losses. Magnetic-soft alloys are employed for alternate magnetization (for instance, in transformer cores).

A special group is alloys which have a high initial magnetic permeability and can be magnetized intensively in weak magnetic fields[1].

Alloying usually makes a metal more hard magnetically.

If an alloying element can only form a solid solution (in iron or another ferromagnetic metal), the magnetic hardness (i.e. the coercive force) increases insignificantly upon alloying. If however, a secondary phase is formed upon alloying above the solubility limit, the coercive force can increase appreciably. The coercive force is higher at a higher dispersity of a secondary phase in an alloy.

Stresses in the crystal lattice caused by strain hardening or phase transformations, and also grain refinement and other deviations from the equilibrium state, can increase the coercive force. This means that structural changes resulting in a higher mechanical hardness can also increase the magnetic hardness (coercive force). This justifies the use of the terms 'magnetic hardness' and 'magnetic softness'.

24.2. STEELS AND ALLOYS FOR PERMANENT MAGNETS (MAGNETIC-HARD ALLOYS)

A material for permanent magnets should have high and time-invariable values of coercive force and remanent induction. The other magnetic characteristics are practically inessential for this group of alloys. Let us consider high-coercive alloys used for permanent magnets.

[1] As can be seen from the initial magnetization curves in Fig. 24.2, alloys of this group should be magnetic-soft.

Carbon steels are used for making permanent magnets of small dimensions. Grades У10 to У12 are employed for the purpose, which upon hardening have H_c = 60-65 Oe and B_r = 8000-8500 Gs.

Chromium steels (1% C and 1.5 or 3.0% Cr) possess approximately the same magnetic properties as carbon steels. They have a higher hardenability and therefore can be used for making larger magnets.

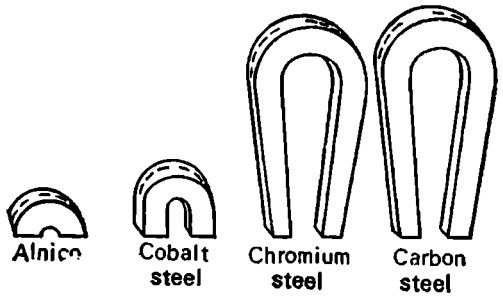

Fig. 24.3. Comparative size of equal-power magnets made of different materials

Cobalt steels (which contain 5 or 15% Co in addition to chromium) possess higher magnetic properties (H_c = 100-170 Oe and B_r = = 8 000-8 500 Gs) than other steels. Cobalt steels have however only a limited application owing to the deficiency of cobalt and because still higher magnetic properties are obtained in less deficient Fe-Ni-Al alloys.

Fe-Ni-Al *alloys* (11-14% Al, 22-34% Ni, and iron the balance), or Alni alloys, ensure a coercive force of 400-500 Oe and the remanent induction 6 000-7 000 Gs. Owing to their high magnetic properties, they can be used to make powerful magnets of rather small dimensions and mass, which is of high importance in instrument-making (Fig. 24.3).

Consider in more detail the particular grades of magnetic steels and alloys for permanent magnets and the conditions of their heat treatment to form a structural state of the highest magnetic properties[1].

Table 24.1. Compositions of Steels for Permanent Magnets, % (GOST 6862—71)

Steel Grade	C	Cr	Other elements
EX	0.95-1.10	1.3-1.6	—
EX3	0.90-1.10	2.8-3.6	—
E7B6	0.68-0.78	0.3-0.5	5.2-6.2 W
EX5K5	0.90-1.05	5.5-6.5	5.5-6.5 Co
EX9K15M	0.90-1.05	8.0-10.0	1.2-1.7 Mo 13.5-16.5 Co

Note. The content of occasional (permanent) impurities is limited at: 0.4% Mn and Si, 0.03% S and P, and 0.3% Ni (or 0.6% Ni in the last two grades).

[1] The highest coercive force in the case considered.

We first consider magnetic steels (Table 24.1). In order to obtain high magnetic properties, steels are subjected to a complex heat treatment consisting of preliminary normalizing (air hardening), quenching from a common hardening temperature in water or oil, and low-temperature tempering (preferably after sub-zero treatment).

The conditions of the heat treatment of magnetic steels and the guaranteed magnetic properties are given in Table 24.2.

Table 24.2. Heat Treatment and Magnetic Properties of Magnetic Steels (GOST 6862—71)

Steel Grade	Heat treatment, °C[1]		Magnetic properties (minimum)	
	air hardening (normalizing), 1st stage	2nd hardening stage[2]	Remanence, B_r, Gs	Coercive force, H_c, Oe
EX3	1 050	840-860	9 500	60
E7B6	1 200-1 250	820-860	10 000	60
EX5K5	1 150-1 200	930-950	8 500	90
EX9K15M	1 200-1 230	1 030-1 050	8 000	150

[1] Freezing at −70°C.
[2] Tempering at 100°C after hardening.

The first, high-temperature stage of air hardening or normalizing is needed to dissolve large carbide inclusions which might form during the prior annealing and which cannot be dissolved in austenite at a common temperature of hardening (as given in the third column of Table 24.2).

Sub-zero treatment can eliminate the paramagnetic retained austenite and thus improve the magnetic properties; tempering at 100°C decreases slightly the coercive force but makes the latter time-invariant.

Steel magnets are made by the same methods as other steel parts, i.e. by forging, followed with annealing and machining.

As has been noted, higher magnetic properties can be obtained by using Fe-Ni-Al alloys which however cannot be machined; because of this, magnets are made of them by casting or by metalloceramic techniques with subsequent grinding.

It has been shown experimentally that the coercive force in Fe-Ni-Al alloys has a maximum at approximately 13% Al; the absolute value of coercive force depends directly on the content of nickel; and it reaches 650 Oe at 30% Ni.

Remanent induction diminishes with increasing nickel content, though the maximum magnetic energy (the product $H \times B$) is obtained at 28% Ni. This is why Fe-Ni-Al alloys usually contain 12-13% Al and have various contents of nickel depending on the required magnetic properties[1]. The compositions of commercial Fe-Ni-Al alloys are given in Table 24.3.

[1] Still higher magnetic properties than those given in Table 24.2 can be obtained in steels with 30% Co (H_c = 250 Oe) and in carbonless age-hardening alloys of the systems Fe-Mo, Fe-V-Co and Fe-Mo-Co. The high content of deficient elements (cobalt and molybdenum up to 30-40%) makes the application of these alloys economically unfavourable, especially after Mishima has discovered high-coercive Fe-Ni-Al alloys.

Table 24.3. Compositions and Properties of Cast Fe-Ni-Al Magnetic Alloys

Name	Alloy Grade	Content of elements[1], %					Magnetic properties (minimum)		
		Ni	Al	Co	Cu	Si	Remanent induction, Gs	Coercive force, Oe	Maximum magnetic energy, Gs Oe×10⁻⁶
Alni 1	ЮН1	22	11	—	—	0.15	7 000	250	0.7
Alni 2	ЮН2	24.5	13.0	—	3.5	0.15	6 000	430	0.35
Alni 3	ЮН3	23.5	15.5	—	4	0.15	5 000	500	0.9
Alnisi	ЮНС	33	13.5	—	—	1.0	4 000	750	1.0
Alnico	ЮНДК12	18	10	12	6	0.15	6 800	500	1.4
Alnico 15	ЮНДК15	20	9	15	4	0.15	7 500	600	1.5
Alnico 18	ЮНДК18	19	10	18	3	0.15	9 000	650	1.7
Magnico	ЮНДК24	13.5	9	24	3	0.15	12 300	500	1.9

[1] Balance iron.

An exceptionally high coercive force of Fe-Ni-Al alloys and their unusual behaviour during heat treatment have been studied more than once. In some cases, these alloys show the maximum coercive force already in as-cast state or upon heating to a temperature between 1 000°C and the melting point and cooling at a controlled rate (for instance 10-20°C/s), see Fig. 24.4*a*. On the other hand, severe quenching gives a reduced coercive force which then cannot be raised by tempering to the value obtained during hardening at a moderate cooling rate (Fig. 24.4*b*). The rate of cooling giving the highest coercive force is called the critical cooling rate.

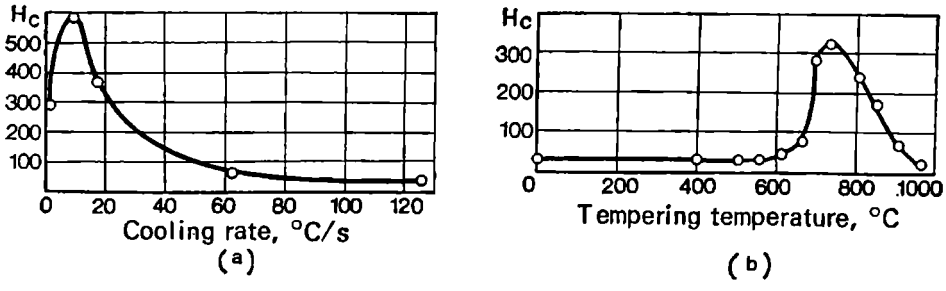

Fig. 24.4. Coercive force of Fe-Ni-Al alloy (27.4% Ni, 14.7% Al)

(*a*) as affected by the rate of quenching rom 1 250°C; (*b*) as affected by tempering temperature (B. G. Lifshits)

By modern views, a high coercive force obtained on hardening should be attributed to the decomposition of the single-phase solid solution in Fe-Ni-Al alloys at high temperatures (on heating for hardening).

The initial single-phase b.c.c. alloy (β-phase) decomposes completely during cooling from a high temperature and forms high-disperse ferromagnetic phases β_1 and β_2 which also have a b.c.c. crystal lattice. These phases differ, however, substantially from each other in composition: β_1-phase is close to iron, while β_2-phase is a solid solution based on NiAl compound. Both phases have a regular crystalline structure.

Since the lattices of these two phases are of the same type and have close lattice parameters, the phases retain a strong coherent bond and a corresponding stressed state at the phase boundaries.

Such a heterogeneous structure consisting of β_1 and β_2 phases with an undisturbed coherent bond possesses the highest coercive force.

Thus, the formation of a high-coercive state reduces to the division of the initial β-phase into high-disperse coherent β_1 and β_2 phases, which results in the appearance of high stresses, distortion of the lattices of the phases, and disintegration of mosaic blocks in the structure. For the most successful course of the process, stepwise decomposition of the β-phase is essential. As has been indicated by B.G. Livshits, there exist two temperature intervals for this stepwise decomposition. In the upper temperature interval (900-800°C), a preliminary process takes place, while in the lower interval (700-600°C), the dispersion decomposition proceeds to its completion.

This state cannot be formed in an alloy by severe quenching and tempering, since quenching fixes the state of the β-phase and inhibits preliminary processes; therefore, only the second stage of the decomposition can occur in the subsequent tempering (at 700-600°C) and coercive force cannot attain its maximum value.

The magnetic properties of Ni-Al alloys are heavily dependent on the mass of magnet and the composition of the metal. For a given composition of the metal, heavier magnets should be cooled more slowly to prevent cracking. The cooling rate may then turn out to be less than the critical value and the metal will not acquire the highest magnetic properties.

The highest magnetic properties are obtained at 27-32% Ni and 12-14% Al (the balance being iron). Nickel increases and aluminium decreases the critical rate of cooling.

Alloys of Ni-Al type with additions of silicon (1-2%) are also used for making magnets. They have a very high coercive force (up to 640 Oe), moderate induction (400-500 Gs), and a reduced critical cooling rate, which is of great importance for making massive magnets. The expensive nickel in Fe-Ni-Al alloys can be partially replaced by copper which also improves somewhat the properties of alloys. For instance, an addition of up to 6% Cu to alloys with 22% Ni increases H_c without lowering B_r. The highest magnetic properties can be obtained by simultaneous alloying with copper and cobalt; the latter increases the coercive force and remanent induction. Special attention should be paid to high-cobalt alloys (15-24% Co) which are subjected to what is called hardening in a magnetic field. The essence of the method consists in that a magnet is heated to the hardening temperature (near 1 300°C) and then placed quickly between the poles of a powerful electromagnet (the field strength should be not less than 120 000 A m) and is cooled there to a temperature below 500°C. Further cooling is usually done in air. The magnet thus treated shows a strong anisotropy of the magnetic properties which turn out to be high only in the direction of application of the external magnetic field during hardening.

Consider the phenomena that can occur during heat treatment in a magnetic field. As is known, the process of transition of an alloy from paramagnetic to ferromagnetic state (at the Curie point) consists in the appearance of regions of spontaneous magnetization in the metal. If a strong magnetic field is applied

to the metal at that moment, microvolumes in the metal will tilt, tending to reorientate along the direction of the external magnetic field, and their tilting will cause plastic deformation in the metal.

The tilting of spontaneous magnetization regions (i.e. plastic deformation) can occur the more easily, the higher the temperature of the metal at that moment, i.e. the higher the Curie point is. The latter can be raised appreciably by the additions of cobalt. This is why magnetic heat treatment gives an appreciable effect in Ni-Al alloys heavily alloyed with cobalt.

Various deformable textured magnetic alloys (such as Vicalloys) have come into use recently. These alloys can be machined quite easily and are manufactured mainly in the form of strips, tape, etc. A Vicalloy-type alloy (52% Co, 14% V, and the balance iron) has a remanent induction of approximately 10 000 Oe and coercive force of 400 Gs.

High-coercive alloys based on rare-earth metal compounds have also found application.

24.3. MAGNETIC-SOFT ALLOYS

There is a large group of magnetic-soft alloys in which the coercive force should be as low as possible, in contrast to magnetic-hard alloys for permanent magnets where a high coercive force is essential.

Whereas a high magnetic hardness is obtained by forming a non-equilibrium high-disperse structure in the metal, a high magnetic softness can be obtained by approaching as close as possible the equilibrium state; it is also essential to form coarse grain and eliminate the sources of lattice distortion and block disintegration.

In addition to a low coercive force, magnetic-soft materials should possess a high magnetic permeability in weak, moderate or strong fields, a low remagnetization loss, etc.

Naturally, pure metals in the first place pure (commercially pure) iron, are most suitable as magnetic-soft materials. In some rare cases, alloys based on iron and also nickel- and cobalt-base alloys are employed for the purpose.

Consider the particular types of magnetic-soft materials.

Commercial iron is practically almost pure iron; all impurities in it, especially carbon, are harmful and their content is strictly limited.

In the USSR, two grades of commercial iron are produced, which differ from each other in the composition and in turn are divided into subgrades according to their magnetic characteristics (Tables 24.4 and 24.5).

The magnetic properties of commercial iron depend on its structural state, as well as on its purity. Strain hardening can sharply impair the magnetic properties of iron. In common commercial grades of iron, the coercive force is of an order of 1 Oe, whereas the lowest coercive force (0.01 Oe) has been obtained in very coarse-grained pure iron.

Table 24.4. Composition of Commercial Iron, % (maximum values)

Iron Grade	C	Mn	Si	S	P	Cu
A	0.025	0.035	0.03	0.025	0.015	0.15
Э	0.040	0.20	0.20	0.030	0.025	0.15

Table 24.5. Magnetic Properties of Commercial Iron

Iron Grade	Magnetic properties	
	coercive force, H_c, Oe	maximum magnetic permeability, Gs/Oe
Э	1.2	3 500
ЭА	1.0	4 000
ЭАА	0.8	4 500

Note. For all iron grades, $B_{10}=15\times10^3$ Gs, $B_{25}=16.2\times10^3$ Gs.

The metal is annealed at a high temperature to form a coarse grain and eliminate the effect of strain hardening. Commercially pure iron is used for making transformer cores, d.c. relays and electromagnets, magnetic screens, poles of electrical machines, etc.

Electric steel is an alloy of ferritic iron and silicon (3% Si, see Fig. 14.6). The iron-silicon solid solution has a higher coercive force than pure iron, owing to the lattice distortions in the iron caused by foreign silicon atoms. A coarse grain can be formed in the alloy by heating, which will not refine on cooling since no $\gamma \rightarrow \alpha$ transformation takes place. This results practically in that the metal has a coercive force not higher than in pure iron. A higher electric resistivity of silicon-alloyed ferrite diminishes eddy current losses.

Electric steel is manufactured in the form of thin sheets which are used for making transformer cores and magnetic parts of electrical machines and d.c. and a.c. electric devices.

As has been noted, electric steel is an alloy of iron and silicon with a strictly limited content of other impurities.

Electric steel sheets are graded according to their thickness, method of manufacture (cold or hot rolled), anisotropy, the main magnetic characteristics (magnetic induction and unit losses), and the content of silicon.

Electric steel sheets are designated by the letter 'Э' and a few digits, the first digit showing the content of silicon[1] (1, 2, 3 or 4 respectively for 0.8-1.8, 1.8-2.8, 2.8-3.8 and 3.8-4.8% Si) and the second, the level of electrical properties (a higher digit corresponding to higher properties). One or two zeroes sometimes written after the digits imply respectively that the steel is cold-rolled textured or cold-rolled low-textured.

For instance, grading Э12 denotes hot-rolled electric steel with 1% Si and with second-class electric properties, grading Э1200 denotes the same steel, but cold-rolled and low-textured.

It follows from the foregoing that only Э3 and Э4 grades are ferritic; they have higher magnetic characteristics but are more brittle. Alloy Grades Э3 and Э4 are called *transformer iron* and Grades Э1 and Э2, *dynamo steel*. In that connection, transformer iron (used mainly in transformer cores) has higher magnetic properties and lower mechanical properties than dynamo steel (which is used mainly in electrical machines).

Crystals of α-iron have a sharply pronounced anisotropy of magnetic properties. Cube edges (ribs) are the axes of the easiest magnetization, so that the formation of a rib texture[2] might increase the magnetic permeability in one direction and lower in the other (perpendicular) direction.

Thus, high magnetic properties can be obtained in Fe-Si alloys of a high purity (especially from carbon) with a coarse grain and textured structure.

The modern technology for making the best grades of electric steel is as follows: a steel of a specified silicon content and a low carbon content (the carbon content is practically obtained at a level of 0.05%) is made in an electric furnace, hot rolled to a thickness of 2.5 mm and then cold rolled into sheets 0.5-0.35 mm thick. Before cold rolling, the metal is annealed at 800°C, which lowers the carbon content to less than 0.02 per cent. After cold rolling, sheets are annealed at 1 100-1 200°C in a hydrogen atmosphere to eliminate the strain-hardening effect and coarsen the grain. If the prior cold deformation was appreciable (45-60%), a textured structure is formed (the degree of texture of an order of 90%); on deformations lower than 7-10 per cent, a low-textured structure is obtained. Finally, if only hot rolling is employed, there will be no texture and the magnetic properties of the metal will be the same both along and across the direction of rolling.

It should be also added that remagnetization losses are lower in thinner sheets. because of which electric steel is mainly manufactured as thin (0.35 or 0.50 mm) sheets.

The magnetic properties of electric steel can be worsened if the metal has been subjected even to a slight plastic deformation during the manufacture of transformer elements (for instance, has been cut or bent).

To restore the magnetic properties it is advisable to subject the final parts to annealing at 750-800°C (which releases stresses and eliminates lattice distortions), followed with slow cooling (at a rate less than 50°C/h).

The properties of selected grades of electric steels are given in Table 24.6.

Iron-nickel alloys (Permalloys) with a content of nickel near 78.5 per cent have an exceptionally high initial magnetic permeability which may reach 10 000 Gs/Oe (Fig. 24.5), i.e. is ten times that of common commercial iron; this circumstance is of great importance for apparatus operating in weak magnetic fields (radio and wire communications, etc.).

[1] With a silicon content above 4.8 per cent, the alloy is so brittle (silicon raises the ductile-to-brittle transition point above room temperature) that it is difficult to be rolled into sheets.

[2] That is, a structure with all crystals oriented similarly.

Table 24.6. Electromagnetic Properties of Electric Steel Sheets

Steel Grade	Magnetic induction,[1] B_{25}, Gs	Unit loss, $P_{10/50}$*	Steel Grade	Magnetic induction,[1] B_{25}, Gs	Unit loss, $P_{10/50}$*
Hot-rolled steel ($\delta = 0.50$ mm)			*Cold-rolled low-textured steel* ($\delta = 0.50$)		
Э11	15 300	3.3	Э1100	15 300	3.3
Э12	15 000	3.2	Э1200	15 300	2.8
Э13	15 000	2.8	Э1300	15 500	2.5
Э21	14 800	2.5	Э3100	15 000	1.7
Э22	14 800	2.2	Э3200	14 800	1.5
Э31	14 600	2.0	*Cold-rolled textured steel* ($\delta = 0.50/0.35$)		
Э32	14 600	1.8	Э310	17 500/17 500	1.1/0.8
Э42	14 500	1.4	Э320	18 000/18 000	0.95/0.7
Э43	14 400	1.25	Э330	18 500/18 500	0.80/0.6

[1] At magnetic field intensity 25 A/cm.
* Upon remagnetization to 10 000 Gs.

The properties of a classical Permalloy (78.5% Ni) depend substantially on heat treatment. The highest initial magnetic permeability can be obtained in it by high-temperature heating in a hydrogen atmosphere (which coarsens grain, removes carbon impurities, and relieves residual stresses). Cooling in a magnetic field improves the magnetic characteristics. The effectiveness of magnetic heat treatment is higher with alloys having a higher Curie point. The method is most effective with alloys containing 77% Ni which have the highest Curie point in the group; their initial magnetic permeability can thus be raised up to 20 000 Gs/Oe.

Alloys of iron and 45-50 per cent nickel (Hypernic type) are also used as magnetic-soft materials. They excel Permalloys without complex heat treatment but are inferior in magnetic properties to heat-treated Permalloys.

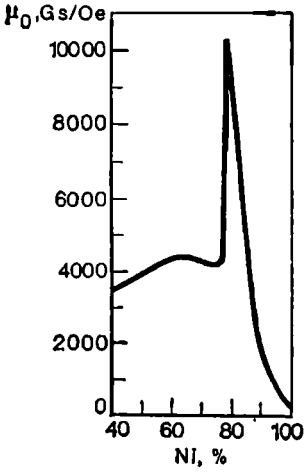

Fig. 24.5. Initial magnetic permeability of Fe-Ni alloys

In addition to binary Fe-Ni alloys just described, use is also made of more complex alloys additionally alloyed with silicon, molybdenum, manganese or copper. These elements increase the electric resistivity of the metal (which allows the metal to be employed at elevated and high frequencies), reduce the sensitivity to strain hardening (this is the effect of molybdenum), and increase the stability of the properties (copper influence).

The magnetic properties of selected Permalloy-type alloys are given in Table 24.7.

In the grading of Permalloys, the two digits indicate the content of nickel (percentage); the letter 'H' is nickel; the letters that follow relate to additional alloying ('X'—chromium, 'C'—silicon, 'M'—molybdenum); a letter 'A' at the end implies a high-quality grade of alloys; otherwise, the alloy is of a common quality.

Table 24.7. Magnetic Properties of Hypernic and Permalloy Alloys

Alloy Grade	Thickness, mm	Magnetic permeability, Gs/Oe		Coercive force H_c, Oe
		μ_0	μ_{max}	
45H	0.35-2.50	2 500	2 300	0.20
	0.20-0.34	2 200	2 000	0.15
	0.10-0.19	1 800	18 000	0.30
	0.05-0.09	1 700	10 000	0.30
50HXC	0.35-1.00	3 200	30 000	0.12
	0.20-0.34	3 000	28 000	0.15
	0.10-0.19	2 500	25 000	0.15
	0.05-0.09	2 000	20 000	0.20
79HM	0.35-2.50	22 000	120 000	0.02
	0.2-0.34	20 000	100 000	0.03
	0.1-0.19	18 000	100 000	0.04
	0.05-0.09	16 000	80 000	0.05
	0.02-0.04	14 000	60 000	0.06
79HMA	0.80-1.00	50 000	300 000	0.01
	0.50-0.70	40 000	300 000	0.01
	0.35-0.49	40 000	250 000	0.01
	0.20-0.34	32 000	150 000	0.02
	0.10-0.19	30 000	120 000	0.03
	0.05-0.09	25 000	100 000	0.05
	0.02-0.04	18 000	80 000	0.06

Other Magnetic-soft Alloys

Alsifer is an alloy in the Al-Si-Fe system which contains 5.4% Al, 9.6% Si, and 85% Fe and has a high magnetic permeability (μ_0 = 35 000 Gs/Oe, μ_{max} = 120 000 Gs/Oe). It is suitable for the same applications as Permalloys which are substantially more expensive. Unfortunately, Alsifer is brittle and cannot be made into sheets; it is mainly used in powder form (for making magneto-dielectrics[1]).

Perminvars are a group of alloys of a constant magnetic permeability. Their magnetic permeability does not vary when the field strength varies from 0 to 80-160 A/m, which is essential in some cases. Examples of Perminvar are: Grade 45 HK (45% Ni, 25% Co, balance iron); 45 HKM (45% Ni, 25% Co,

[1] In recent time, magnetic ferrites (Oxifers), which are metallic oxides of M_3O_4 type, have come into a wide use as high-permeable materials. They however possess no metallic properties, belong to semiconductors and for that reason are not discussed in the book.

7.5% Mo, balance iron); 70 HK (70% Ni, 7% Co, balance iron). The initial magnetic permeability of these alloys is respectively 365, 850, and 550 Gs/Oe and the maximum permeability, 1 800, 4 000, and 3 800 Gs/Oe.

Permendur is an alloy (50% Co, 1.8% V, balance iron) having a high saturation induction. It is used in instruments in cases where a powerful flux of the lines of force should be concentrated in a small volume. The magnetic saturation of Permendur is 23 800 Gs, compared to 21 500 Gs of iron.

Thermalloy is an alloy whose induction varies substantially in the temperature range from —60° to +50°C; it is used in devices for the automatic correction of moving-coil instruments. Such a strong variation of the magnetic properties of the alloy is due to the fact that its Curie point is very close to (slightly above) that temperature interval. A certain practical application have found alloys of iron with 30% Ni (Thermalloy) and with 30% Cu (Calmalloy).

Since the saturation induction and the Curie point are structure-insensitive characteristics, the principal working properties of Permendur and Thermalloy alloys are independent of heat treatment and are determined only by the alloy composition.

24.4. NON-MAGNETIC STEELS

Some materials for electrical engineering should be non-magnetic ($\mu < 1.05$) and have a high mechanical strength. Instead of non-ferrous metals, less expensive non-magnetic austenitic steels are used for the purpose. Austenitic stainless (see Ch. 19) or wear-resisting (see Ch. 20) steels can be used as non-magnetic materials provided that they have an appropriate strength. However, steel Grade Г13 often turns out to be unsuitable because of its low strength or poor technological properties, while austenitic stainless steels are too expensive to be used in large-mass parts (for instance, in non-magnetic bandage rings of turbogenerators). In such cases use is made of steels alloyed with manganese, chromium and aluminium at a relatively high content of carbon (near 0.4%) and a limited content of nickel.

An austenitic structure is formed by hardening and the strengthening effect is provided by cold work hardening (if the strength of as-hardened steel is insufficient). The austenitic structure in the steel should be stable, i.e. the *Md* point should be below 0°C, since otherwise a deformation at room temperature might form martensite.

The compositions of selected commercial non-magnetic steels are given in Table 24.8.

At an earlier time, high-nickel steels (such as Grade ЭН269) were used as non-magnetic. At present, compositions have been found, which are lower in deficient nickel (55Г9Н9Х3) or are even nickel-free (45Г17Ю3) in which manganese serves as an austenite-forming element. In this respect, manganese is

Table 24.8. Compositions of Non-magnetic Steels, %

Steel Grade	C	Mn	Cr	Ni	Other elements
ЭИ269	0.50-0.60	4.0-5.5	0.25	18.5-21.5	—
55Г9Н9Х3	0.58-0.68	7.5-9.5	3.0-4.0	7.5-9.5	0.5-1.0 W
45Г17Ю3	0.40-0.50	16.0-18.0	0.50	0.50	2.5-3.2 Al

two times less efficient than nickel, because of which the carbon content in a steel is increased to form a stable austenite. In a nickel-free steel, an austenitic structure and non-magnetism can be obtained at a composition of 0.4% C and 17% Mn. This is a Hadfield-type steel which has an inherent disadvantage of being substantially strain-hardenable, and therefore, it cannot be easily plastic worked, machined, etc. The strain-hardening susceptibility of manganese-alloyed austenitic steels can be suppressed appreciably by the additions of aluminium.

These specifics of alloying of high-manganese austenite with aluminium are utilized in a less expensive steel Grade 45Г17Ю3. Its mechanical properties in as-hardened state are as follows: $\sigma_t = 70$ kgf/mm², $\sigma_{0.2} = 35$ kgf/mm², $\delta = 35$ per cent, $a_{nI} = 10$ kgf m/cm². The ultimate strength can be raised by work hardening to 150-180 kgf/mm², but this lowers the ductility. All the austenitic steels mentioned are not corrosion-resisting, though their corrosion resistance is higher than that of common carbon steels. In applications where non-magnetic steels of a high corrosion resistance are required, use should be made of stainless steels (type X18H12) or non-ferrous metals (brasses).

24.5. STEELS AND ALLOYS WITH SPECIAL ELECTRIC PROPERTIES

The magnetic and electric properties of a metal are closely interrelated, as they are due to the same physical phenomena. This is why steels and alloys with special electric properties are discussed in the chapter on magnetic alloys. Steels of this group can have either a low resistance to the passage of current or, on the contrary, a high resistance. The former are used for energy transmission and the latter, for converting electric energy into heat.

Pure metals: copper, aluminium and, less frequently, silver and iron, are preferably used as conductors, since alloying (and strain hardening) of a pure metal causes lattice distortions and thus increases the electric resistivity.

Resistance elements, on the contrary, should have a low electric conductivity. This is why alloys, but not pure metals, are used for the purpose. These alloys are used in rheostats (*resistance alloys*) and in the heating elements of various electric heating devices and electric furnaces (these are called *high-resistance alloys*).

If two components of an alloy can form a mechanical mixture, the electric resistivity of the alloy varies by an additive law (see

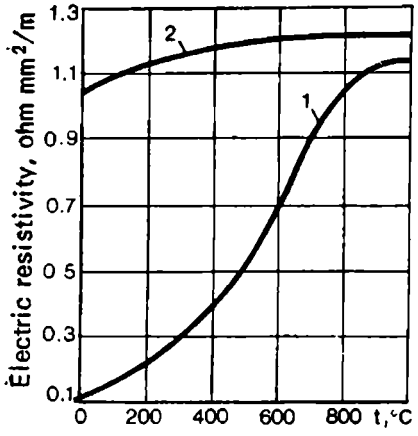

Fig. 24.6. Effect of temperature on the electric resistivity of (*1*) iron and (*2*) Nichrome

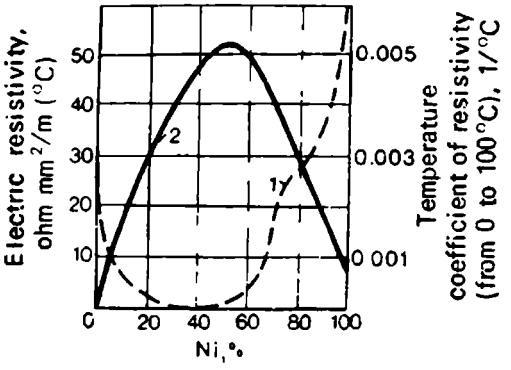

Fig. 24.7. Electric properties of Cu-Ni alloys

1 — temperature coefficient of resistivity; *2* — resistivity

Fig. 5.43*a*). When components form solid solutions, the resistivity varies by a curvilinear relationship and is usually higher than that of the pure components (see Fig. 5.43*b*). Hence it follows that high-resistance elements should be made of alloys in which the constituent metals form solid solutions; these alloys are usually solid solutions of a high concentration.

High-resistance alloys should possess the following properties:

1. A high electric resistivity.

2. A low temperature coefficient of resistivity, i.e. their resistivity should vary only slightly with temperature. The resistivity of metals, such as iron, increases with temperature (Fig. 24.6). Evidently, a rheostat can control the current accurately if the resistivity of its alloy changes only slightly with temperature (as for instance in Nichrome).

3. A high scale resistance. This property is not very essential in rheostats where the wire is heated only to 300-500°C, but is of high importance in, and determines the service life of, electric heating elements which operate at appreciably higher temperatures.

Resistance alloys are mostly alloys of copper with nickel, zinc or manganese; such are Nickelines, Constantans, and Manganins.

Copper and nickel are completely soluble in each other in the solid state. Copper-nickel alloys with 40-50% Ni show the highest electric resistivity in the group and an almost zero temperature coefficient of resistivity (i.e. their resistivity does not practically vary with temperature, Fig. 24.7).

The compositions and properties of selected resistance alloys are given in Table 24.9.

Iron, silicon, lead, sulphur, carbon, phosphorus, and arsenic are harmful impurities in these alloys and their content is limited.

It is interesting to note that resistance alloys have an electric resistivity four to five times that of iron (0.1 ohm mm²/m) whereas their temperature coefficient of resistivity is only a few hundredths of that of iron (0.006), see Table 24.9.

Table 24.9. Composition (%) and Properties of Resistance Alloys

Alloy Grade	Ni	Mn	Impurities (total)	Properties		
				resistivity at 20°C, ohm mm²/m	temperature coefficient of resistivity	maximum working temperature, °C
МНМц3-12 (manganin)	2.5-3.5	11.5-13.5	<0.9	0.43	0.000 03	200
МНМц40-1.5 (constantan)	39-41	1-2	<0.9	0.48	0.000 02	500
МНМц43-0.5 (copel)	42.5-44.0	0.1-1.0	<0.6	0.50	0.000 14	500

Note. The alloys also contain copper (to make the balance).

High-resistance alloys are usually iron- or nickel-base alloys; the former are called Nichromes.

Table 24.10 gives the compositions of selected high-resistance alloys, and also the values of their resistivity and maximum working temperature (i.e. the temperature at which the intensity of oxidation becomes inadmissibly high).

Table 24.10. Composition (%) and Properties of High-resistance Alloys

Alloy Grade	Name	C	Si	Mn	Cr	Ni	Al	Resistivity at 20°C, ohm mm²/m	Temperature coefficient of resistivity (×10⁻⁵)	Maximum working temperature, °C
Х13Ю4	Fechral	0.15	0.1	0.7	12-15	0.6	3.5-5.5	1.26	5	1 000
1Х17Ю5	Alloy No. 1	0.12	0.2	0.7	16-19	0.6	4.6-6.0	1.30	1	1 000
1Х25Ю5	Alloy No. 2	0.12	1.2	0.7	23-27	0.6	4.5-6.5	1.40	—	1 150
Х20Н80	Nichrome	0.15	0.4-1.3	0.7	20-23	75-78	0.2	1.11	1	1 100
Х15Н60	Nichrome	0.15	0.4-1.3	1.5	15-18	55-61	0.2	1.10	1.7	1 050

High-resistance alloys low in chromium and aluminium and having the scale resistance up to 1 100°C are manufactured in the form of wire[1]. Those high in chromium and aluminium (such as Megapyr alloys) have the scale resistance up to 1 250-1 350°C, but are brittle, so that resistor elements are made of them by casting.

[1] Though nickel-free alloys have a higher scale resistance than Nichromes, the latter often show a higher stability in operation, probably owing to their higher ductility and also to the fact that wire made of them is usually free of defects (cracks, fissures, turns, etc.). In the presence of defects, the electric resistivity may increase locally, resulting in the local overheating and a lower stability of a heating element.

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Chapter 25

ALLOYS FOR NUCLEAR ENGINEERING

25.1. EFFECT OF IRRADIATION ON METAL PROPERTIES

Metals in the structures of nuclear reactors are irradiated by various elementary particles formed during the reactor operation. These particles, in particular, fast neutrons, penetrate deep into the metal and change its properties.

The elementary particles that penetrate into the crystal lattice of metal, especially fast neutrons which carry no electric charge and therefore do not interact electrically with electrons and protons, knock out metal atoms from their regular sites in the crystal lattice, and these in turn can knock out other atoms encountered on their path. It has been shown theoretically that a neutron can knock out up to 300 atoms in aluminium. Such strong distortions produce defects in the crystal lattice of the metal.

In addition, lattice defects can form owing to thermal peaks. The point is that part of the energy of neutrons is spent to excite elastic oscillations in individual groups of atoms. This corresponds, as it were, to a sharp rise of temperature in a small volume. The heat is quickly dissipated from these places (by conduction) and the metal is hardened locally which is associated with strong residual distortions of the lattice.

These defects inhibit dislocation movement and thus produce a strengthening effect in the metal. In the general, nuclear irradiation resembles work hardening in its effect.

For instance, nuclear irradiation can increase the strength of plain steels 1.5 to 2 times and accordingly diminish the ductility and toughness. The effect of nuclear irradiation on a metal strengthened by common methods (work hardening, hardening) is less appreciable than on as-annealed metal. The effect of nuclear irradiation decreases with rising temperature and is practically absent at temperatures above the recrystallization point.

It should be remembered that nuclear irradiation can form atoms of other elements owing to nuclear fission or to the capture of neutrons by the base metal atoms. Upon a long irradiation, a pure metal may change to an alloy owing to the transformation of some of its atoms into other elements.

Finally, an irradiated metal becomes radioactive and dangerous for the man's health.

25.2. STRUCTURAL MATERIALS. HEAT CARRIERS

Nuclear engineering employs very diverse materials: structural steels, stainless and heat-resisting steels and alloys, non-ferrous metals, etc. All the materials used in nuclear engineering should however have some special properties not required in other branches of industry. In the first place, their atom nuclei should be capable of absorbing thermal neutrons (low-energy neutrons). Some materials, such as those for biological protection or for controlling fission reactions in piles, should have a high capacity for absorbing neutrons, while others should have a low capacity (for instance, shells of fuel elements in atomic piles). The neutron-absorbing capacity of various metals varies over wide ranges (Table 25.1).

Table 25.1. Effective Neutron-capture Cross-section and Melting Point of Selected Metals

Properties	Be	Mg	Zr	Al	Fe	Ni	Hf	B	Cd
Effective neutron-capture cross-section, barn*	0.01	0.063	0.18	0.23	2.4	4.5	115	720	2 400
Melting point, °C	1 280	651	1 845	660	1 539	1 455	2 130	2 000	321

* 1 barn = 10^{-24} cm².

The elements in the right portion of the table are most effective for making screens for neutron protection. Those in the left portion can be used as structural materials in reactors.

Magnesium and aluminium are often unsuitable for this purpose owing to their low melting point and are replaced by beryllium and zirconium.

Beryllium. Since the effective neutron-capture cross-section of metals does not depend on their state, beryllium is employed in nuclear engineering in the metallic state and as compounds with oxygen, carbon and hydrogen (beryllium oxides, carbides and hydrides).

Commercial beryllium is a brittle metal of an ultimate strength of about 30 kgf/mm² and elongation of 1-2 per cent. Its low plasticity may be due to insufficient purity, since the metal is very sensitive to impurities. Its corrosion resistance is high. As a structural material, it will be discussed later in the book.

In view of the low effective neutron-capture cross-section, high melting point and high corrosion resistance, beryllium can be used in shells of fuel rods[1], though its extremely high cost prevents its wide application. A less expensive metal, zirconium, is now used successfully for this purpose.

[1] Beryllium is also used as a source of neutrons on bombardment with α-particles, in 'windows' of X-ray tubes (it is transparent to X-rays), and in some other cases.

Zirconium. Owing to its low neutron-capture cross-section, high melting point, and high values of ductility and corrosion resistance, zirconium has found a preferable application in fuel rod shells and as coating of pipes. Zirconium has two allotropic modifications: h.c.p. α-form and b.c.c. β-form. The temperature of $\alpha \rightleftarrows \beta$ transformation is 862°C. The mechanical properties of zirconium may vary, depending on the purity, structural state and other factors, within the following limits: σ_t = 20-40 kgf/mm², $\sigma_{0.2}$ = 5-20 kgf/mm², δ = 20-40 per cent, and hardness 30-60 *HB*. As may be seen, it is a rather soft and weak metal. Zirconium can be strengthened substantially by alloying. Some zirconium alloys are known to have an ultimate strength σ_t = 80-100 kgf/mm² (at a lower ductility, δ = 3-5%), such as Zircalloy (0.5-1% Sn, 0.2% Fe, and 0.3% Ni).

The corrosion resistance of zirconium is heavily dependent on its purity. Carbon and nitrogen lower its corrosion resistance appreciably in concentrations of a few hundredths of a per cent. Some additions can however neutralize the harmful effect of impurities (for instance, niobium neutralizes the effect of carbon and tin, the effect of nitrogen). Since zirconium undergoes phase transformations, the properties of zirconium alloys can be changed by heat treatment. There are still no sufficient data on the heat treatment of zirconium alloys and the associated structural changes, though constitutional diagrams have been obtained for many zirconium systems.

Commercial zirconium is usually contaminated with hafnium (commonly some 2%). Hafnium is its neighbour in the Periodic Table and has similar properties, except for the effective neutron-capture cross-section which is 1 000 times higher. For that reason, zirconium for its principal application should be purified from hafnium, which is a rather difficult problem and increases appreciably its cost. For other applications (i.e. not in nuclear engineering), this purification is needless, since hafnium does not affect the mechanical and chemical properties of zirconium.

Zirconium is also employed as a gas absorber (getter), in surgery[1], and in metallurgy (for alloying and deoxidizing).

Heat carriers. Heat transfer in nuclear reactors is effected by means of liquid-metal heat-carriers which are more effective than water or gases owing to their higher heat conductivity. The metals to be used as heat carriers should naturally have a low melting point. Depending on the type of reactor, use is commonly made of bismuth (and its alloys) and sodium.

In some types of nuclear reactors, the heat carrier contains dissolved nuclear fuel (uranium) and should therefore have a low melting point (practically not above 500°C) and be capable of dissolving uranium.

As may be seen from Table 25.2, among all light metals, bismuth is the best suitable for the purpose.

A further circumstance of importance is that bismuth has a low capacity for absorbing thermal neutrons.

Instead of pure bismuth, it is quite feasible to use a Pb-Bi eutectic which contains 43.5% Pb and 56.5% Bi and has a melting point at 125°C (Fig. 25.1*a*). The addition of lead makes the alloy less expensive and more fluid (owing to the lower melting point). The eutectic has a somewhat lower capacity for dissolving uranium and a higher neutron absorptivity (see Table 25.2), though within tolerable limits.

Of great importance is the interaction of bismuth (or Bi-Pb alloy) with the

[1] Like tantalum and in contrast to such materials as silver or silk, zirconium does not interact with living tissues.

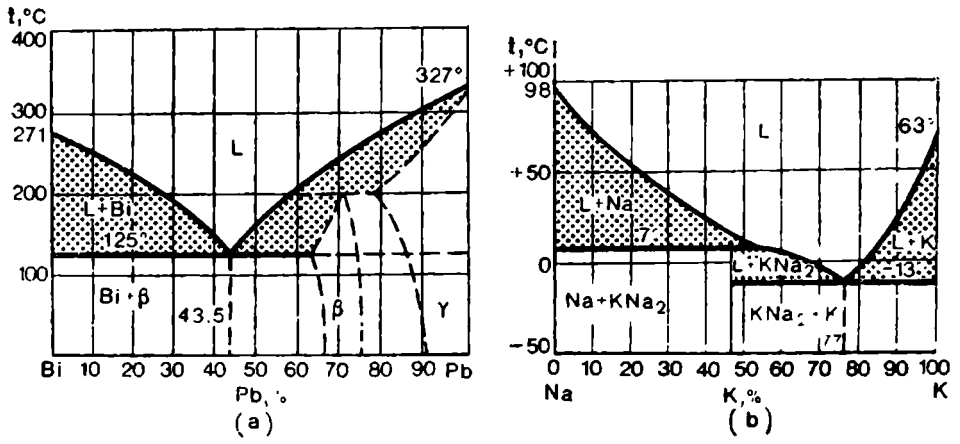

Fig. 25.1. Constitutional diagrams
(*a*) Bi-Pb; (*b*) Na-K

Table 25.2. Physical Properties of Non-ferrous Metals

Property	Zn	Ga	In	Tl	Sn	Pb	Sb	Bi
Melting point, °C	419	30	156	303	232	327	630	271
Solubility for uranium at 900°C, % (at.)	0.32*	0.90**	0.51	0.13	0.2	0.52	1.5	12.3
Effective neutron-capture cross-section, barn	1.06	2.7	190	3.3	0.65	0.17	6.40	0.03

* At 500°C.
** At 700°C.

metals of heat-exchanger tubes. The stability of various metals in this medium is quite different and depends on temperature.

Platinum, manganese and nickel are utterly unstable in liquid bismuth, and the stability of copper and aluminium is not much better. Plain non-alloyed iron and carbon steel retain their stability at higher temperatures (750°C) than stainless steels. Beryllium and molybdenum are stable at temperatures up to 1 000°C. Thus, the common concepts on the corrosion stability of various metals are inapplicable in that case.

The heat of nuclear fission in reactors can be transferred effectively by light metals; in their thermal properties they substantially excel water, since they have a higher latent heat of vaporization (i.e. can absorb more heat), a lower vapour pressure (i.e. a system can operate at a lower pressure and have thinner walls), a higher heat conductivity, etc.

Table 25.3. Physical Properties of Alkali-earth Metals

Substance	$T_{m.p.}$, °C	$T_{b.p.}$, °C	Latent heat of vaporization, kcal/kg	Vapour pressure[1], mm Hg	Heat conductivity[2], kcal/m h °C	Density at 20°C, g/cm³
Lithium	179	1 317	4 680	400	35	0.53
Sodium	98	883	1 005	400	75	0.97
Potassium	64	760	496	400	40	0.86
Rubidium	39	688	212	400	30	1.53
Water	0	100	539	760	0.58	1.0

[1] At temperatures of 600-800°C (except for lithium).
[2] At temperatures of 100-200°C.

Among the light metals given in Table 25.3, only rubidium has found no application as yet, probably because of its rare occurrence. Sodium, and also potassium which is much like sodium in its properties, are used most often, while lithium is employed less frequently.

Sodium is very soft at room temperature (deforms between fingers) and can be easily cut by a knife.

In nuclear reactors, sodium is used in pure form or as an alloy with potassium (44% K), Fig. 25.1*b*. The alloy is liquid at room temperature, which offers certain technological advantages. The thermal conductivity of the alloy is slightly less than that of pure sodium.

Various metals have different resistance to the corrosive action of liquid sodium. A high stability is shown by nickel, chromium, molybdenum, iron, and zirconium; titanium and stainless steel are partly stable and carbon steel, aluminium, and platinum are unstable. Austenitic steel and zirconium which possess the optimum combination of properties satisfy best the modern technological requirements.

The corrosion stability of metals, especially of iron alloys, decreases sharply if the sodium contains even a slight concentration of oxygen. This is why liquid sodium and Na-K alloys should be thoroughly purified from oxygen.

25.3. NUCLEAR FUEL (URANIUM, PLUTONIUM, AND THORIUM)

Less common metals: uranium (U), thorium (Th), and plutonium[1] (Pu) have now become important as fuel for the production of atomic energy.

Uranium in the form it occurs in nature is a mixture of at least two isotopes: 99.3% U^{238} and 0.7% U^{235}.

Nuclear fission of uranium atoms (of its isotope U^{235}) liberates an enormous quantity of energy. In contrast to U^{235}, the other isotope, U^{238}, is not fissioned by neutron bombardment. On capturing neutrons, U^{238} transforms to another

[1] Plutonium is not found in the Earth's crust; it is an artificial element obtained by neutron bombardment of uranium.

isotope, U^{239}, which on loosing a β-particle transforms into neptunium (Np, atomic number 93), and the latter forms plutonium (atomic number 94) on losing another β-particle. On neutron bombardment, plutonium is fissioned and liberates energy; thus, plutonium can serve as a substitute for U^{235} isotope.

Uranium is a silvery-bright metal of a density of around 19.0 g/cm³, i.e. one of the heaviest metals.

It is not oxidized in air at room temperature, but burns at a rather low temperature (170°C). The melting point of uranium is 1 132°C.

Uranium has three allotropic modifications: U_α with an orthorhombic crystal lattice, which is stable below 668°C; U_β with a tetragonal lattice, stable within 668-720°C; and U_γ with a b.c.c. lattice, stable above 720°C.

Thus, the transformation points of uranium are as follows: 668°C ($\alpha \rightleftarrows \beta$), 720°C ($\beta \rightleftarrows \gamma$), and 1 132°C ($\gamma \rightleftarrows L$). Other elements are almost insoluble in U_α and can only be present as compounds, but are noticeably soluble in U_β and U_γ; therefore, uranium alloys can be heat treated by heating to the β or γ state to dissolve the excess phase and then by fast cooling which can fix a state that is stable at a high temperature or some intermediate states; for instance, it is possible to obtain a disperse mixture U_α + secondary phase or a supersaturated U_α solution by the martensitic reaction.

Single crystals of U_α exhibit a marked anisotropy of their properties, especially of thermal expansion. For instance, the coefficient of linear expansion of crystals may be 22×10^{-6} in one direction and 1.5×10^{-6} in another (i.e. a U_α crystal expands in one direction and contracts in another when being heated).

Rolling, especially cold rolling[1], produces a deformed texture in uranium. Crystals are oriented preferably in one direction, so that the properties of the metal become anisotropic and depend on the direction of testing. Hardening with heating above the $\alpha \rightarrow \beta$ transformation point causes misorientation of crystals and eliminates or diminishes the anisotropy.

The mechanical properties of uranium are rather low: hardness near 220 *HB*, $\sigma_t \approx 36$ kgf/mm², and $\sigma_{0.2} \approx 23$ kgf/mm². The proportionality limit of uranium is astonishingly low, only 2 kgf/mm². Different orientation of grains, grain size, purity, and other factors may have an appreciable effect on the mechanical and other properties of uranium.

The mechanical properties of uranium change appreciably on irradiation. For instance, uranium specimens upon losing 0.035 per cent (at.) of their mass through fission have shown a strength only one-fourth of the initial value and their relative elongation diminished from 17 per cent to 0.36 per cent, whereas the hardness has risen from 220 to 300 *HB*.

Plutonium. Despite its low melting point (640°C), plutonium has six allotropic modifications (their stability limits are given in brackets): α (119°C), β (119-218°C), γ (218-310°C), δ (310-450°C), η (450-472°C), and ε (472-640°C). Thus, plutonium has the greatest number of allotropic modifications among metals.

All plutonium modifications solve almost no elements (including manganese, iron, nickel, beryllium, lead, vanadium, and chromium), because of which impurities of these elements do not affect the points of allotropic transformations of plutonium.

All metals are known to expand on heating; δ and η modifications of plutonium are abnormal in that respect: they contract on heating.

Studies of plutonium are difficult to be conducted because of the high radioactivity of this element and require special radiation protection (experiments

[1] The recrystallization temperature of uranium is near 450°C, so that rolling below that temperature may be regarded as cold rolling.

are usually carried out in 'hot boxes' with the use of remote-controlled instruments).

Thorium. Naturally occurring thorium metal is not a fissionable material, but can be transformed into a nuclear fuel, U^{233}, by neutron bombardment.

Thorium has two allotropic modifications: f.c.c. Th_α and b.c.c. Th_β. The temperature of $\alpha \rightleftarrows \beta$ transformation is 1 400°C. The melting point of thorium is 1 775°C and its density, 11.7 g/cm³.

The anisotropy of the properties of thorium crystals is not so marked as with uranium, because of which thorium does not change its dimensions as strongly as uranium in cyclic heating.

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Part Five

NON-FERROUS METALS AND ALLOYS

Chapter 26

LIGHT METALS AND ALLOYS

Light metals are those which have a low density, less than 3 g/cm³. If we exclude alkali-earth metals which also have a low density, the group of light metals will consist of only three metals: aluminium, magnesium, and beryllium. They will be discussed in this chapter.

The principal physical properties of these metals are given in Table 26.1.

Table 26.1. Principal Physical Properties of Light Metals

Properties	Al	Mg	Be
Atomic number	13	12	4
Atomic mass	27.0	24.3	9.0
Relative density at 20°C, g/cm³	2.7	1.7	1.8
Melting point, °C	660	651	1 284
Boiling point, °C	2 327	1 107	2 450
Atomic diameter, Å	3.2	2.8	2.3
Latent heat of melting, cal/°C	94	46.5	275
Heat conductivity at 20°C, cal/cm s °C	0.54	0.38	0.45
Coefficient of linear expansion at 25°C, deg	24.3×10^{-6}	26.0×10^{-6}	11×10^{-6}
Electric resistivity at 20°C, ohm cm	2.7×10^{-6}	4.5×10^{-6}	3.6×10^{-6}
Normal modulus of elasticity E, kgf/mm²	7 100	4 570	30 000

ALUMINIUM AND ITS ALLOYS

Among the three light metals, aluminium is of the highest importance owing to its low cost and large production scale (second only to iron).

In 1808, H. Davy, an English scientist, predicted the existence of aluminium, the constituent of common clay, and gave it its name.

First particles of aluminium were obtained by H. Oersted of Denmark in 1825.

The modern method for making aluminium (by electrolysis from molten salts) was invented independently and patented by Ch. Hall of the USA and P. Héroult of France in 1886.

Up to 1890, only 200 t of aluminium were manufactured in the world and the cost of aluminium was only slightly less than that of gold. In the following decade, 28 000 t of aluminium were produced and in 1930, 27 000 t. Now, the annual world production of aluminium (excluding the USSR) is near 10 mln t.

Aluminium was used only in pure form up to 1906 when A. Wilm of Germany discovered quite occasionally a method for strengthening Al-Cu alloys by hardening and ageing and the alloy proposed by him (4% Cu, 0.5% Mg, and 0.5% Mn) is now the most popular aluminium alloy (duralumin). In modern engineering, aluminium is employed as structural material mostly in the form of alloys, in the first place as duralumin which has a high strength (σ_t = 30-60 kgf/mm^2) and low density (2.6-3 g/cm^3).

26.1. THE PROPERTIES OF ALUMINIUM

The most typical characteristics of pure aluminium are a low density (γ = 2.7) and a low melting point (660°C). Its density is almost one-third that of iron (γ = 7.8). In view of this, aluminium and its alloys are widely used in cases where a low density and a high strength are essential. Since the melting point of aluminium is appreciably lower than that of iron, the technology of processing aluminium differs greatly from that for steels.

The most typical characteristics of pure aluminium are a high ductility and a low strength. Rolled and annealed aluminium of high purity has the following properties: σ_t = 6 kgf/mm^2, $\sigma_{0.2}$ = = 2 kgf/mm^2, hardness 25 *HB*, ψ = 85 per cent, and δ = 40 per cent*.

Aluminium has a face-centred lattice with lattice parameter of 4.04 Å at 20°C and its atomic radius is 1.43 Å. It has no allotropic modifications and possesses high values of heat and electric conductivity and a very high latent heat of melting.

Despite its close affinity for oxygen, aluminium is only weakly oxidized in air and some other media, which is explained by the formation of a dense film of Al_2O_3 which prevents further corrosion.

* That is, it is close in its properties to purest iron; it may be said in general that various metals of the highest purity differ only slightly from one another in mechanical properties.

The corrosion resistance of aluminium worsens with increasing content of impurities.

The purest (extra-pure) aluminium, see Table 26.2, contains 99.999% Al and the sum of all impurities is not more than 0.001 per cent; it is used preferably in laboratory experiments. For industrial applications, high-purity (99.995-99.15% Al) or commercial-purity aluminium (99.85-99.0% Al) is employed depending on the particular requirements. The grading of pure aluminiums may be seen from Table 26.2.

Table 26.2. Primary Aluminium Grades (GOST 11069—74)

Grade	Al, % (minimum)	Impurities, % (maximum)		
		Fe	Si	total
		Extra-high purity		
A999	99.999	—	—	0.001
		High purity		
A995	99.995	0.001 5	0.001 5	0.005
A99	99.99	0.003	0.003	0.010
A97	99.97	0.015	0.015	0.030
A95	99.95	0.030	0.030	0.050
		Commercial purity		
A85	99.85	0.08	0.06	0.15
A8	99.8	0.12	0.10	0.20
A7	99.7	0.16	0.16	0.30
A6	99.6	0.25	0.20	0.40
A5	99.5	0.30	0.30	0.50
A0	99.0	0.50	0.50	1.0

The principal (permanent) impurities in aluminium are iron and silicon; their effect will be discussed in the next section.

Aluminium is not good as structural material in view of its low strength, but its plasticity, corrosion resistance and electric conductivity can be utilized effectively in some special applications[1]. Thus, there are three ways for the application of commercial aluminium:

(1) owing to its high plasticity, aluminium suits well for deep stamping and rolling to a small thickness (for instance, it is rolled to foil to be used in food industry);

(2) its high conductivity (65 per cent that of copper) allows it to be used in electrical engineering (as conductor). For a given con-

[1] Especially if we take into account that it has a low cost per unit mass or per unit volume.

ductivity, aluminium wire conductors are lighter than those made of copper;

(3) aluminium finds wide application in cases where its high corrosion resistance can be utilized. It is a chemically active metal, but initial oxidation forms a dense oxide film (of a thickness of approximately 100 Å) which isolates the metal from the surroundings. This circumstance makes aluminium highly corrosion-resisting. Aluminium is practically quite stable in organic acids (and for that reason is widely used in domestic appliances and for the transportation and storage of foodstuffs).

Aluminium can withstand the action of inorganic acids only in low concentrations.

26.2. PERMANENT IMPURITIES IN ALUMINIUM (IRON AND SILICON)

Figure 26.1 shows the aluminium-rich corner of the Al-Fe constitutional diagram. Iron can be considered to be practically insoluble in aluminium[1], so that even a slight content of iron forms an Al + Al_3Fe eutectic which contains only 1.7% Fe (or 7% Al_3Fe). Because of the low content of iron, the eutectic coalesces and its typical structure cannot be revealed by microexaminations. The structure of Al-Fe alloys consists of aluminium and dark Al_3Fe inclusions (Fig. 26.2).

Silicon forms no compounds with aluminium. The Al-Si constitutional diagram is shown in Fig. 26.3. The solubility of silicon in aluminium is very low and it can be taken, therefore, that pure silicon is present in the Al-Si system. The solubility of silicon in aluminium is 1.65 per cent at the eutectic temperature

[1] By the latest data, the solubility of iron in aluminium at the eutectic temperature (655°C) is approximately 0.03 per cent.

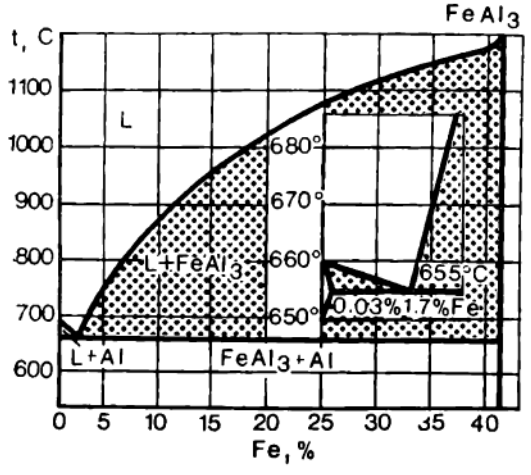

Fig. 26.1. Portion of the Al-Fe constitutional diagram

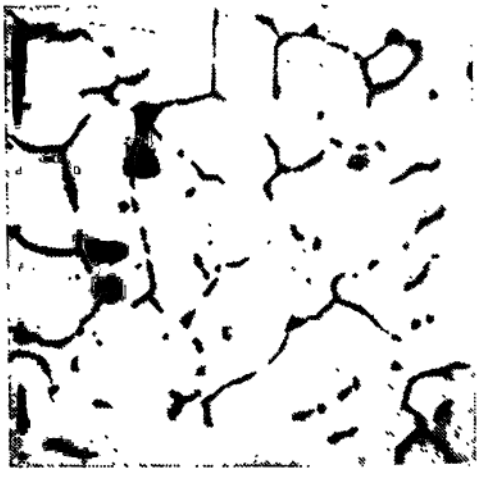

Fig. 26.2. Structure of cast commercial aluminium. Dark Al_3Fe inclusions. × 200

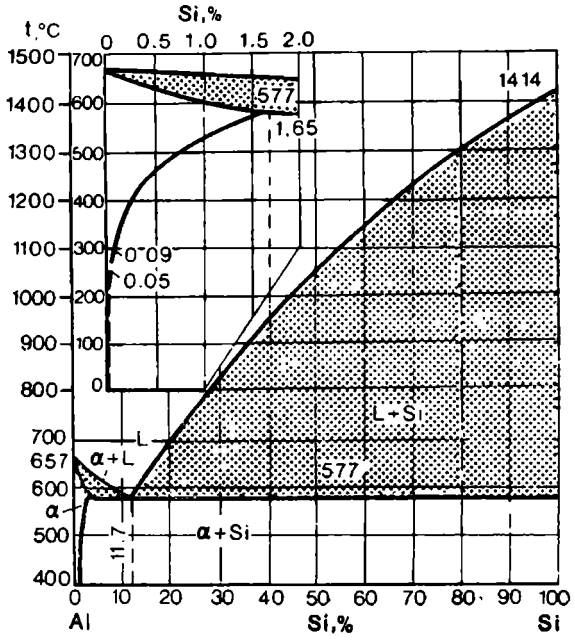

Fig. 26.3. Al-Si constitutional diagram

and almost zero at room temperature (0.09% at 300°C). The eutectic contains 11.7% Si and consists of alternating inclusions of the two phases (see Fig. 26.21).

With both silicon and iron present in aluminium, there appear new phases which are not found in binary alloys; these are ternary compounds of iron, silicon and aluminium which may be designated as α (Al-Fe-Si) and β (Al-Fe-Si).

Thus, an alloy can contain the phases Al_3Fe, α (Fe-Al-Si), β (Al-Fe-Si), and silicon, depending on the content of silicon and iron.

These compounds, especially when formed on the grain boundaries, diminish the plasticity of aluminium.

26.3. HEAT TREATMENT OF Al-Cu ALLOYS *

The strengthening heat treatment of aluminium alloys is based on changes in the solubility of alloying compounds in the aluminium base solution, in particular for Al-Cu alloys, in the solubility of $CuAl_2$ compound.

As may be seen from Fig. 26.4, the solubility of copper in aluminium at room temperature is around 0.2 per cent and the maximum solubility at the eutectic temperature (548°C) is 5.7 per cent. Any alloy with up to 5.7% Cu can be made single-phase by proper heating[1] and this state can be fixed by quick cooling.

* Heat treatment of steels has been discussed in the book on the basis of Fe-C alloys. In aluminium alloys, copper is the second most important element, because of which Al-Cu alloys are taken as an example for discussing the structural transformations in the heat treatment of aluminium alloys. The picture remains principally the same if other elements are introduced in addition to, or in place of, copper.

[1] That is, secondary crystals of $CuAl_2$ can be transferred fully into the α-solid solution.

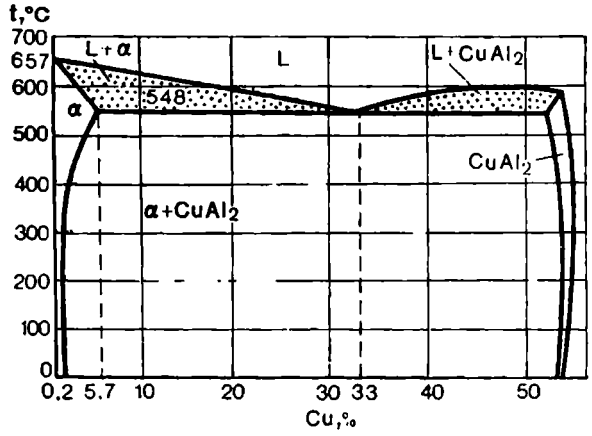

Fig. 26.4. Al-Cu constitutional diagram

The rate of cooling on hardening is determined by the rate of precipitation of excess phases from the undercooled supersaturated solid solution. For this purpose it is advisable to construct a diagram of isothermal transformation of the undercooled solid solution (C-curve), such as that shown in Fig. 26.5. As is seen from that diagram, the highest rate of transformation is observed near 300°C.

A solid solution thus obtained will be supersaturated if its copper content is more than 0.2 per cent. It is unstable and may undergo certain transformations resulting in the precipitation of $CuAl_2$, so that the remaining solid solution contains an equilibrium content of copper (0.2%). This process is called *ageing*[1], and more particularly, *natural ageing* if it occurs at room temperature and *artificial ageing* if it takes place on an artificial increase of temperature. Thus, the heat treatment of aluminium alloys has two stages: hardening and ageing.

The theoretical problems associated with the hardening of aluminium alloys are quite simple: the hardening process should fix the state of supersaturated solid solution. It is important to carry out cooling as quickly as possible.

The phase changes upon hardening can be well illustrated by the microstructures of alloys.

Figure 26.6*a* and *b* shows the microstructures of an aluminium alloy Grade A17 (4% Cu) as annealed, which consist of $CuAl_2$ in-

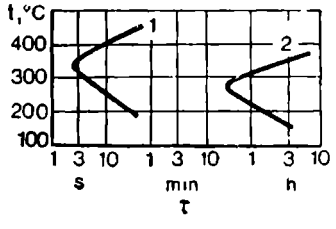

Fig. 26.5. Diagram of the isothermal decomposition of undercooled solid solution in aluminium alloys (beginning of decomposition)

1 — Al + 4% Cu + 1.5% Mg; *2* — Al+ 4% Zn + 2% Mg

[1] Ageing implies all the processes occurring in a supersaturated solid solution, both the processes prior to precipitation and precipitation proper. A transformation in which only precipitation processes occur is called *precipitation hardening* (without the complex preliminary processes which will be discussed later).

Fig. 26.6. Structures of an Al + 4% Cu alloy
(*a*) as annealed. ×900; (*b*) ditto. ×100; (*c*) as hardened. ×100

clusions on the background of the solid solution of aluminium (almost pure aluminium). Figure 26.6*c* shows the microstructure of the same alloy upon hardening, which is a homogeneous solid solution. Heating to the temperature of hardening resulted in complete dissolution of $CuAl_2$ inclusions and the subsequent cooling fixed the supersaturated solid solution (as may be judged from the microstructure).

Let us now consider how the properties of Al-Cu alloys vary during ageing.

The ultimate strength of an as-annealed Al + 4% Cu alloy is $\sigma_t = 20$ kgf/mm^2. In a just-hardened state (i.e. if tested immediately on hardening), the ultimate strength is slightly higher (approximately 25 kgf/mm^2). Upon ageing, it increases appreciably and reaches 40 kgf/mm^2.

In natural ageing (at 20°C) the ultimate strength reaches a maximum in four or five days after hardening. The rate of strengthening is first (during the first few hours) not high, then increases to a maximum and after that gradually decreases.

The typical shape of the strengthening curve in natural ageing is shown in Fig. 26.7.

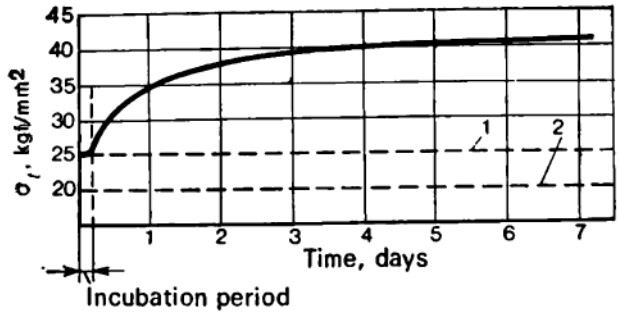

Fig. 26.7. Strength variations in the natural ageing of an aluminium alloy
1 — as hardened; *2* — as annealed

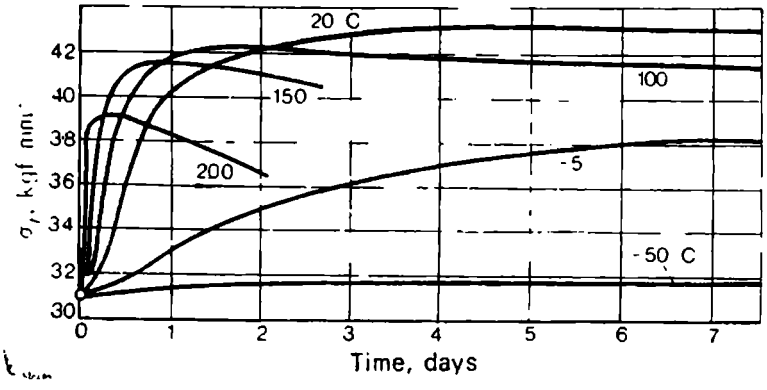

Fig. 26.8. Ageing curves of duralumin at various temperatures

The initial period during which the strength increases insignificantly or even does not rise at all is called the *induction period*. It is of great importance from the technological standpoint, since at that period an alloy can be easily deformed plastically, and therefore, hardened parts can be deformed by various technological processes (driving of rivets, bending, flanging, etc.). In two or three hours, the capacity of the metal to plastic deformation decreases abruptly and these operations become unfeasible[1].

The rate of ageing depends appreciably on temperature (Fig. 26.8), being higher at higher temperatures. The maximum strength thus obtained is however lower at higher temperatures of ageing[2]. In addition, ageing at a temperature above 150°C can result in a noticeable softening of an alloy, which occurs more quickly at higher temperatures.

At temperatures below 20°C ageing is slowed down and it may be taken that no ageing occurs at temperatures below —50°C and that the hardened state is practically stable.

A naturally aged alloy is structurally unstable. If a naturally aged aluminium alloy is held for a short time at 200-250°C, it will soften and acquire the properties typical for its state just after hardening, i.e. it again becomes capable of being naturally aged (Fig. 26.9). This phenomenon, i.e. the restoration of as-hardened state after a short heating is called *recovery*.

We have considered the changes in an alloy which take place on ageing (see also Sec. 5.10). What are the processes that cause these changes?

Let us analyse the processes of ageing in Al-Cu alloys.

Hardening fixes the state of supersaturated solid solution, so that

[1] The time of induction period is different for various alloys; besides, it depends on the temperature of the surroundings.

[2] This is true not for all aluminium alloys.

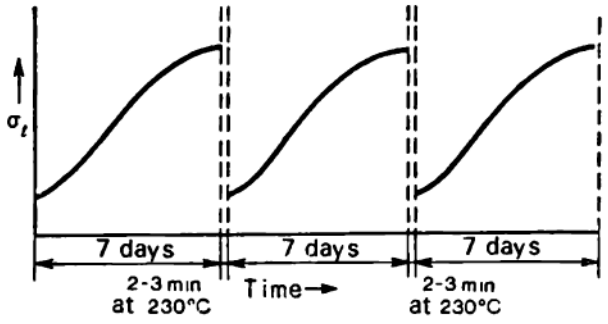

Fig. 26.9. Ageing curves upon recovery to as-hardened state (short heating at 230°C)

it is most probable that a disperse excess phase ($CuAl_2$) precipitates in ageing and causes changes in the properties of the alloy.

This theoretical assumption is not however supported by the available experimental data. Microstructural analysis reveals no difference between the hardened and aged state of an aluminium alloy, i.e. the second phase is not seen in the microscope.

The second phase (i.e. that precipitated from the solid solution) can be clearly revealed upon artificial ageing at a temperature above 200°C (Fig. 26.10). However, an alloy in which the second phase can be detected metallographically does not show the maximum strength, since the time of ageing (tempering) was much longer than that needed to form the maximum strength (at a given temperature of ageing).

Thus, metallographic analysis disproves the simple hypothesis of precipitation of excess phase. Maybe, the point is that precipitated particles are so fine that cannot be seen in the microscope? X-ray structural analysis also shows that an aged alloy at its highest strength contains no excess phase[1].

It follows from the foregoing that no precipitation in the common sense occurs in natural ageing and that the strengthening effect is not associated with decomposition of the solid solution.

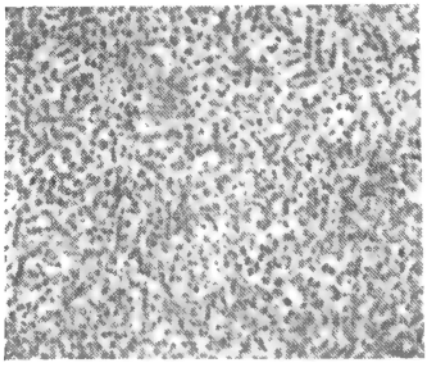

Fig. 26.10. The structure of Al + 4% Cu alloy upon hardening and artificial ageing at 250°C. ×900

With artificial ageing, precipitation actually takes place only at tempera-

[1] When present in the solid solution of aluminium, copper diminishes [the lattice parameter, since its atomic radius is 1.28Å and that of aluminium, 1.43 Å. Precipitation of copper from the solid solution should increase the lattice parameter, whereas actually the lattice parameter is not changed on ageing. Only at temperatures above 200°C the lattice parameter increases, which is associated with the precipitation of a second phase from the solution; this can also be detected by other methods (for instance, metallographically).

tures above 200°C and a holding time which does not ensure the maximum strength; this is confirmed by various methods of physico-chemical analysis.

The modern view on the mechanism of ageing, which is confirmed by the method of X-ray structural analysis, is as follows: during natural ageing, certain preliminary processes take place whereas the precipitation proper can only occur at high temperatures which ensure a sufficiently high rate of atomic displacement (diffusion).

The initial period of ageing (let it be called the first stage of ageing) consists in that the atoms of a second component (copper atoms in the case considered), which have occupied random places in as-hardened alloy, are collected in definite places of the crystal lattice. The process results in the formation of zones with an elevated concentration of the dissolved component in a crystal; these are called *Guinier-Preston (G.P.) zones*[1].

At this stage of ageing, copper atoms do not precipitate, and therefore, the average value of the lattice parameter is not changed. In places of increased concentration of the second component, the parameter should be not the same as in depleted places; this causes high stresses in a crystal and disintegrates mosaic blocks, and therefore, increases the hardness.

Guinier-Preston zones are thin lamellar disc-shaped formations a few atomic layers thick and a few tens of atomic layers long[2].

G.P. zones have an elevated copper content, which however does not correspond yet to the formula $CuAl_2$.

In the further process, Guinier-Preston zones increase in size (up to 10-40 Å in thickness and 200-300 Å in diameter) and their copper content rises to the stoichiometric ratio. The initial small Guinier-Preston zones are usually called G.P.-1 zones and the larger ones, G.P.-2 zones, though there is no principal difference between the two. The process associated with the formation[3] of G.P. zones is also called *zone ageing* (I.N. Fridlander) to distinguish it from the subsequent stage which is called *phase ageing*.

Upon the formation of G.P.-2 zones, a higher temperature or a longer holding time at an elevated temperature, say 100°C, causes these zones to transform into a phase denoted as θ′. This is a precipitated phase, i.e. its lattice differs from those of the solid solution and the stable θ-phase ($CuAl_2$), but has a coherent bond with the solid solution of the matrix. With a further increase in temperature, the θ′-phase changes to the stable θ-phase and coagulates.

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[1] After A. Guinier of France and G. D. Preston of Great Britain who independently (in 1938) discovered these processes in ageing of duralumins.

[2] The following dimensions have been given: thickness 5-10 Å and diameter 40-100 Å.

[3] The term 'precipitation' is inapplicable in this case; the term 'preprecipitation' is often used.

In simple Al-Cu alloys with 3-5% (or in similar alloys with a slight content of magnesium—duralumins), zone ageing occurs at room temperature and gives the maximum strengthening effect (see Fig. 26.8); at temperatures of 100-150°C, zone ageing changes to phase ageing which cannot form the highest strength. At still higher temperatures (200°C), θ′-phase degenerates into θ-phase (or θ-phase forms directly from the solid solution) which still gives a lower strengthening effect (see Fig. 26.8).

G.P. zones formed at various temperatures are different in size, so that small G.P. zones that have formed at room temperature are unstable at higher temperatures (say, at 200°C) and are 'resolved' ('dissolved'), since larger G.P. zones are stable at that temperature. Therefore, if a naturally aged alloy is heated to 150-200°C, the former small-size zones will be dissolved and the alloy returns to the state it had just after hardening. This explains the phenomenon of recovery.

To conclude the discussion of ageing processes, the following circumstances should be noted. Firstly, an aged state with G.P. zones does not always correspond to the maximum of strength; in many alloys, the maximum of strength is observed on the formation of metastable θ′-phase.

Secondly, the process should not necessarily pass through all the three stages: G.P. $\rightarrow \theta' \rightarrow \theta$; it may start directly from the precipitation of θ′-phase or even of θ-phase.

Thirdly, the division of ageing into natural (at 20°C) and artificial (at higher temperatures, say 100-150°) is purely technological, but not physical. The physical classification considers the processes occurring during ageing and from that standpoint a distinction should be made between zone ageing and phase ageing. For duralumins (4% Cu, 0.5% Mg), natural ageing is the same as zone ageing and artificial ageing is the same as phase ageing. In other alloys, precipitated phases can form already at room temperature; in still other alloys no ageing (strengthening) occurs at room temperature.

26.4. EFFECT OF COMPOSITION OF ALUMINIUM ALLOYS ON HEAT TREATMENT PROCESSES

We consider now the effect of copper and other elements on the properties of binary Al-Cu alloys and on their heat treatment.

The curves in Fig. 26.11 show that the hardness of Al-Cu alloys depends on the content of copper. The effect of ageing, i.e. the differences in the hardness of an alloy in as-hardened and aged state (the upper curve in the diagram) gradually increases with increasing copper content; alloys with up to 2% Cu do not practically age, since the supersaturation in them is still insufficient to give an appreciable change in the properties during ageing.

The highest strengthening effect during ageing is obtained at 6% Cu, which roughly corresponds to the solubility limit of copper in aluminium at high temperature (see Fig. 26.4).

Contamination of an alloy with iron diminishes the effect of ageing. This action of iron is due to the formation of a ternary Cu_2FeAl compound (called *N*-phase) which is almost insoluble in aluminium.

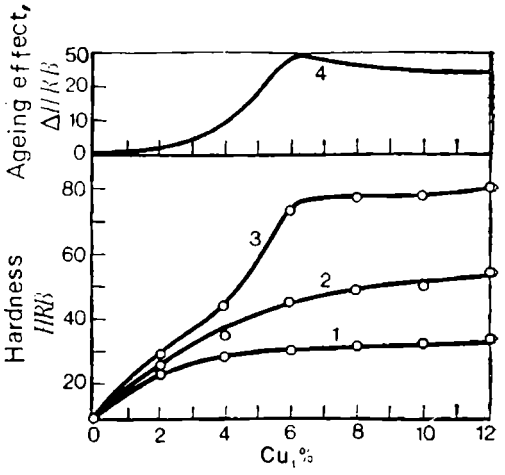

Fig. 26.11. Effect of copper on the hardness of Al-Cu alloys

1 — as annealed; *2* — as hardened; *3* — on ageing to the maximum strength. Curve *4* shows the effect of strengthening in ageing, i.e. the difference between the aged and as-hardened state. The tested alloys contained 0.2-0.3% Fe and 0.03-0.09% Si

The higher is the iron content in an alloy the more copper is spent to form the ternary compound and the less is the quantity of the soluble $CuAl_2$ compound which determines the strengthening effect of heat treatment. Fig. 26.12 shows the microstructures of as-hardened Al + 4.5% Cu alloys with various contents of iron. A higher content of iron gives a higher percentage of insoluble iron compounds (black inclusions in Fig. 26.12). Thus, iron is a harmful impurity in age-hardening Al-Cu alloys[1].

Aluminium can form solutions of variable solubility not only in the Al-Cu system, but also when melted together with many other elements, so that these alloys can be strengthened by hardening and ageing. Such elements are silicon, magnesium, zinc, and some others

[1] The harmful effect of iron diminishes in the presence of magnesium.

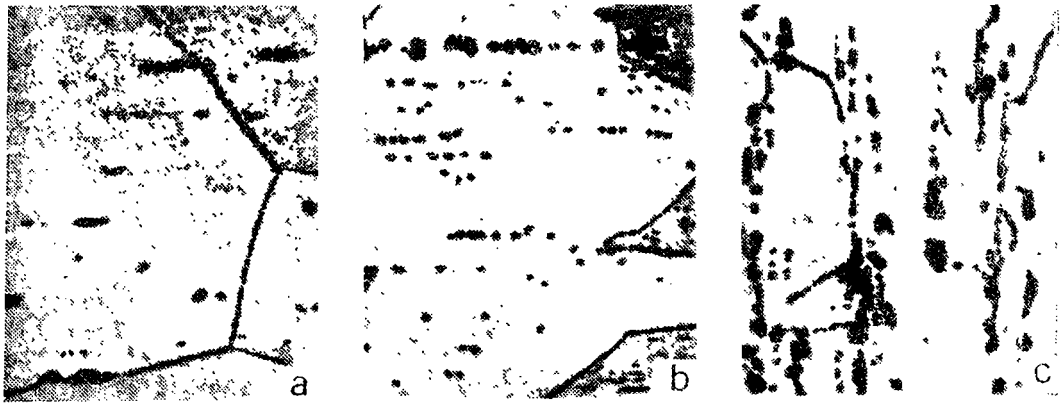

Fig. 26.12. Structures of Al + 4.5% Cu alloys as hardened. ×400. Iron content, %
(*a*) 0.1; (*b*) 0.63; (*c*) 1.06

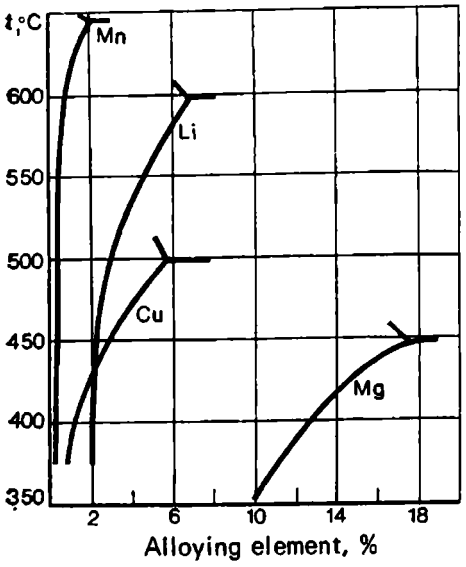

Fig. 26.13. Curves of solubility of selected elements (in solid state) in aluminium

(Fig. 26.13). This is why modern age-hardening aluminium alloys are alloyed with silicon, magnesium, zinc and lithium, as well as with copper.

In binary Al-Cu, Al-Si, Al-Mg

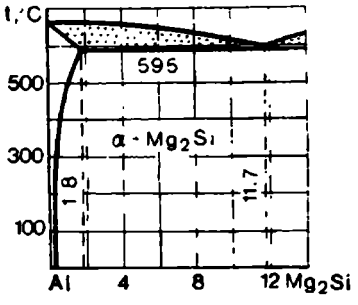

Fig. 26.14. Al-Mg_2Si system

and Al-Zn alloys, the effect of heat treatment is less profound than in ternary or more complex alloys, because of which complex aluminium alloys have found a wider application than binary alloys.

Among ternary and quarternary aluminium alloys, the following systems have found the widest application:

1. Alloys of the Al-Mg-Si system, called Avials. In these alloys, Mg_2Si compound forms a phase that is dissolved on heating for hardening and precipitates in ageing and produces the strengthening effect (Fig. 26.14). To obtain the maximum strengthening effect in these alloys by heat treatment (at Mg : Si = = 1 : 2), the total quantity of Si + Mg should be around 2 per cent.

2. Alloys of the Al-Cu-Mg system (*duralumins*). Depending on the copper content and the copper-to-magnesium ratio, these alloys can contain either binary compounds $CuAl_2$ or Al_3Mg_2 (at a low content of one of the elements, either magnesium or copper) or ternary compounds $CuMgAl_2$ (called *S*-phase) and $CuMg_5Al_5$ (*T*-phase). These compounds have a varying solubility in aluminium. Figure 26.15 shows the aluminium-rich corner of the ternary Al-Cu-Mg system. Line *a-b* is the solubility limit of copper and magnesium at room temperature and line a_1-b_1 is the solubility limit at a high temperature. Therefore, alloys with the concentrations of copper and magnesium between these lines form homogeneous solid solutions on heating and can be strengthened by heat treatment. The diagram shows the phases that are formed in these alloys on annealing, and therefore, it is possible to determine the phases that are dissolved and give the strengthening effect on heat treatment.

As has been established by D.A. Petrov et al., the dissolution of *S*-phase in subsequent ageing gives the highest strengthening effect compared to the other phases in the system. For that reason, alloys near line a_1-b_1 (between points *x* and *y*) are most capable of being strengthened by heat treatment in the Al-Cu-Mg system; they are called high-strength duralumins.

3. Alloys of the systems Al-Cu-Li and Al-Mg-Li.

Lithium, a light metal from the alkali-earth group, has only recently come into use as an alloying element for aluminium alloys. Studies on the Al-Li

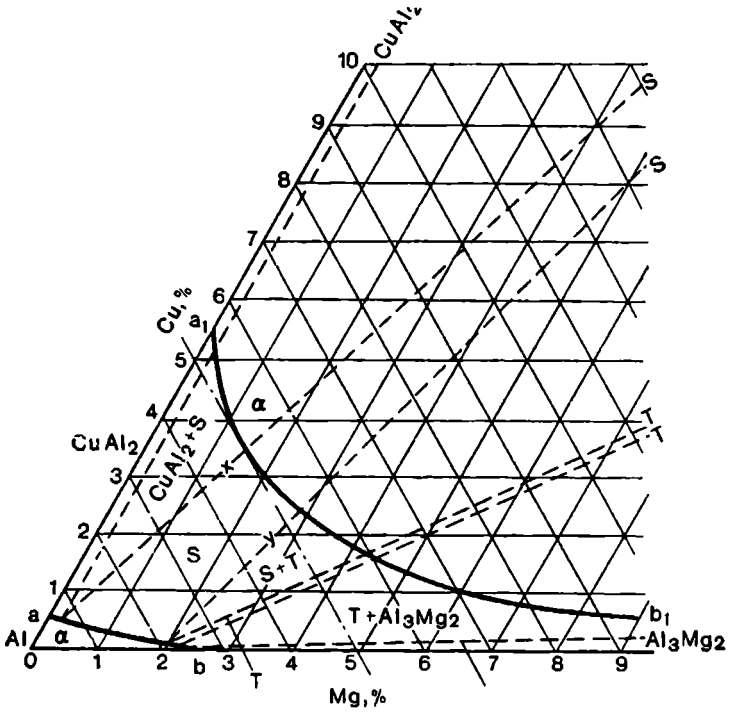

Fig. 26.15. Aluminium-rich corner of the Al-Cu-Mg constitutional diagram (G.G. Urazov and D.A. Petrov)

system (see Fig. 26.13) have established a high solubility of LiAl compound in aluminium, which also is heavily dependent on temperature; this offers the possibility of strengthening by heat treatment. Binary Al-Li alloys have turned out to be ineffective (owing to a relatively low strengthening effect produced by heat treatment and a high oxidation on heating), but ternary Al-Cu-Li and Al-Mg-Li alloys are quite valuable in practice.

The Al-Cu-Li system is shown in Fig. 26.16*a* from which it may be seen that the strengthening effect in ternary alloys can be due to one of the following phases: T_b ($Al_{15}Cu_8Li_2$), T_1 (Al_2CuLi) or T_2 (Al_6CuLi_3).

Phase T_1 is similar in its nature to S-phase (Al_2CuMg) in the Al-Cu-Mg system and gives the highest strengthening effect on dissolution, which increases in the presence of a small quantity of cadmium (0.1-0.2%)*.

Alloys of the Al-Mg-Li system are the lightest among aluminium alloys, since both alloying elements (magnesium and lithium) decrease the density of an aluminium alloy and ageing is due to the precipitation (more strictly, pre-precipitation) of lithium-containing ternary phases.

4. Alloys of the Al-Zn-Mg system. Like magnesium, zinc has a high solubility in aluminium at high temperatures (400°C) and a low solubility at low temperatures (below 200°C). The same, but in a stronger form, is typical of the $Al_2Mg_3Zn_3$ compound, called T-phase (see Fig. 26.16*b*) which is isomorphous to

* Cadmium does not affect the strength of as-annealed or as-hardened alloys, but increases the strength in aged alloys. It is interesting that cadmium, which is an inert alloying element in the classical Al-Cu-Mg system, does not affect the properties of the alloys of this system. This shows that the effect of an alloying element in some alloys or under particular conditions may be absent in other alloys or under different conditions.

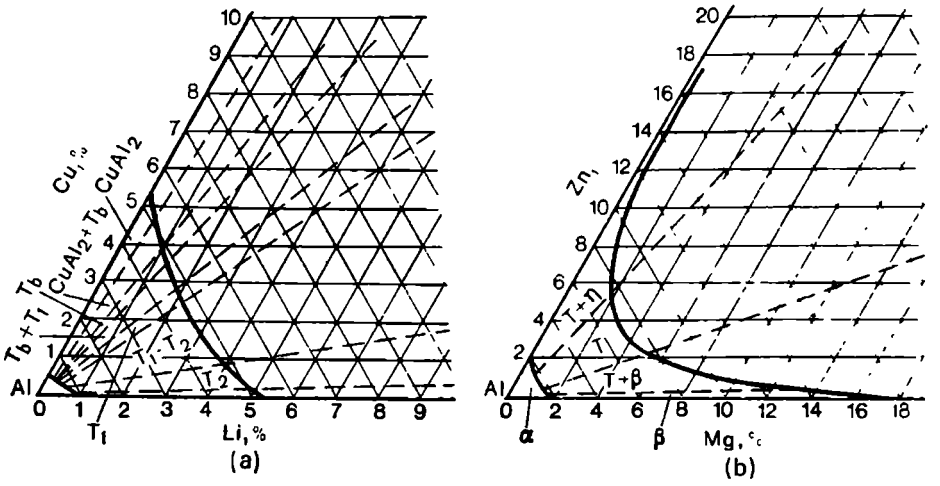

Fig. 26.16. Aluminium-rich corner of (*a*) Al-Cu-Li system and (*b*) Al-Zn-Mg system

the *T*-phase of the Al-Cu-Mg system. Alloys of this system allow a heavy alloying, which gives a deep supersaturation on hardening and the best properties on ageing.

Table 26.3 gives the phases which are dissolved on heating, i.e. which cause ageing, and the phases (zones) whose formation produces the maximum strengthening effect of ageing in various alloy systems.

Table 26.3. Phases and Zones in Aluminium Alloys

System	Phases causing strengthening effect on heat treatment	Metastable zones and phases appearing on heat treatment	Strengthening effect discovered	
			in	by
Al-Cu-Mg	θ ($CuAl_2$) *S* (Al_2CuMg)	G.P.-1, G.P.-2; θ′	1906-11	Wilm
Al-Mg-Si	β (Mg_2Si)	G.P.; β	1915-21	Geiler
Al-Zn-Mg	η ($MgZn_2$) *T* ($Al_2Mg_3Zn_3$)	Zones; η′	1923-24	Sander Meissner
Al-Zn-Mg-Cu	η ($MnZn_2$) *T* ($Al_2Mg_3Zn_3$)	Zones; η′	1932	Weber
Al-Cu-Mn	θ ($CuAl_2$) *T* ($Al_{12}Mn_2Cu$)	G.P.; θ″; θ′	1938 1950	Petri Phragmen
Al-Cu-Li	θ ($CuAl_2$) *T* ($Al_{7.5}Cu_4Li$) T_1 (Al_2CuLi)	θ′: T_1	1956	Hardy, Sealcock
Al-Li-Mg	*S* (Al_2LiMg) δ (AlLi)	δ′ (Al_3Li)	1968	I.N. Fridlander et al.

26.5. CLASSIFICATION OF ALUMINIUM ALLOYS

Commercial aluminium alloys are divided into two groups: those employed in the deformed state (pressed, rolled or forged) and casting alloys. The boundary between the two groups determines the saturation limit of the solid solution at the eutectic temperature (see Fig. 26.18).

An analysis of the process properties of alloys with reference to their constitutional diagram (Fig. 26.17) shows that alloys in which the content of a component is below the solubility limit at a high temperature possess the highest ductility and the least strength at high temperatures, and therefore, are suitable for hot plastic working.

The presence of a eutectic structure sharply lowers the ductility, pressability, rollability and forgeability and at a definite content of the eutectic (usually slight), plastic working becomes impossible.

The best fluidity is exhibited by metals which crystallize at a constant temperature (pure metals, eutectic alloys). After having passed beyond the solubility limit at high temperature, the fluidity increases abruptly.

The total volume of casting voids varies gradually, but their size and distribution depend on the temperature interval of crystallization. With a large temperature interval, casting voids are usually small and are distributed over the whole cross-section of a casting. The density of that casting is low, but the casting shrinkage will also be low for the same reason. With a zero temperature interval of crystallization (pure metals or eutectic), a large shrinkage cavity forms in a definite place of the casting; by the proper arrangement of casting gates, it can be shifted into the riser and thus a casting of a high density can be obtained.

The concentration of alloying components in casting alloys should exceed the solubility limit at high tempera-

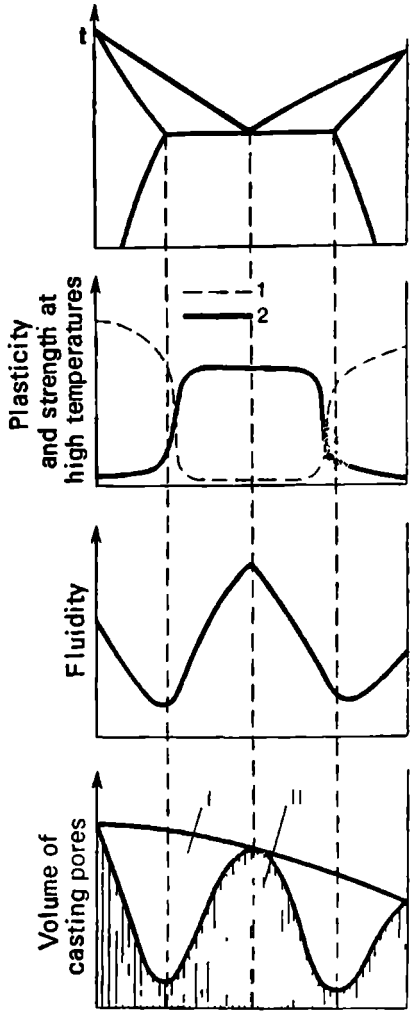

Fig. 26.17. Process properties of binary systems with limited solubility of the components (A.A. Bochvar)

1 — plasticity; *2* — strength; *I* — distributed voids; *II* — concentrated voids

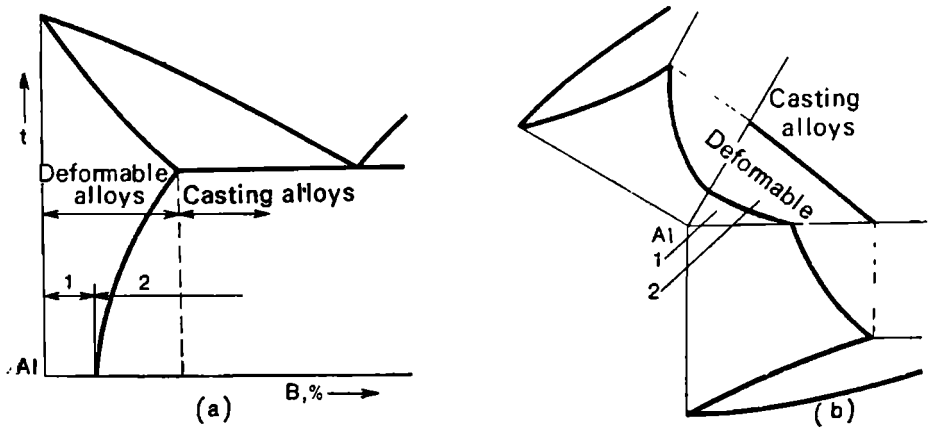

Fig. 26.18. Classification of aluminium alloys by the constitutional diagram (*a*) binary system; (*b*) ternary system; *1* — alloys which cannot be strengthened by heat treatment; *2* — those which can be strengthened by heat treatment

ture, firstly, for a sufficient strength to be formed to prevent cracking due to internal stresses (natural and inevitable) in as-cast (not annealed) part; this is also needed to increase the fluidity of the metal.

Thus, referring to the constitutional diagram (Fig. 26.18), aluminium alloys can be divided into casting and deformable alloys. On the other hand, casting alloys should not contain too much of the eutectic (more than 15-20% by volume), otherwise their mechanical and some process properties would be impaired. All casting alloys can be strengthened by heat treatment, but the strengthening effect is lower at a heavier alloying, i.e. when the structure contains more of the eutectic.

Deformable alloys are subdivided into those which can be strengthened by heat treatment and those which cannot. Theoretically, the boundary between these two groups should be the saturation limit of the solid solution at room temperature, but practically even the alloys which contain alloying elements in an amount slightly above that limit cannot be strengthened by heat treatment since they contain an insufficient quantity of the strengthening phase.

The division of real alloys into casting and deformable in the constitutional diagram is however conditional, since these alloys do not reach the equilibrium in as-cast state and their structures differ from the equilibrium structure (see Sec. 5.10).

26.6. DEFORMABLE ALLOYS WHICH CANNOT BE AGE-HARDENED BY HEAT TREATMENT

These alloys can be characterized by a relatively low strength[1] and high values of ductility and corrosion resistance. They are

[1] Only slightly higher than that of pure aluminium.

employed in cases where a high ductility is essential, for instance, for deep stamping.

The group includes alloys of the systems Al-Mn (Grades АМц) and Al-Mg (Grades АМг). They cannot be age-hardened by heat treatment.

Though the Al-Mn system (see Fig. 26.13) exhibits a variable solubility of Al_6Mn compound in aluminium, in the presence of iron (which is an inevitable impurity) there forms a ternary $Al_6(Mn, Fe)$ compound which is insoluble in aluminium.

Unlike other elements which impair the corrosion resistance of aluminium alloys, manganese has a positive effect on this characteristic. This is why Al-Mn alloys excel pure aluminium both in strength and in corrosion resistance.

Al-Mg alloys with the magnesium content up to 1.4 per cent cannot be strengthened by heat treatment (which follows from the solubility curve in the Al-Mg system, see Fig. 26.13). At a higher content of magnesium (above 3%), age-hardening is possible, but the strengthening effect is not high.

Magnesium is a useful alloying element in aluminium alloys. In addition to its positive effect on corrosion resistance[1], it also lowers the density of aluminium alloys (since it is lighter than aluminium), increases the strength, and has no effect on ductility. Thus, Al-Mg alloys have found application as being stronger and lighter than pure aluminium.

The compositions of Soviet-made АМг and АМц alloys employed in aircraft engineering are given in Table 26.4.

Table 26.4. Average Compositions of Deformable Alloys Not Strengthened by Heat Treatment, % (GOST 4784—74)

Alloy Grade	Mn	Mg	Alloy Grade	Mn	Mg
АМц	1.0-1.6	<0.05	АМг5	0.3-0.6	4.8-5.5
АМг2	0.2-0.6	1.8-2.8	АМг7	0.5-0.8	5.8-6.8
АМг3	0.3-0.6	3.2-3.8			

Note. In most of these alloys, Si $<$ 0.4-0.6%, Fe $<$ 0.5-0.7%, and Cu $<$ 0.2-0.5%.

These alloys are delivered as sheets or shaped rolled or pressed sections in as-annealed (soft) state (designated by the letter 'М' in the alloy grading), in a slightly work-hardened state, i.e. semi-work-hardened (designated with the letter 'П') or in a strongly work-hardened state (designated with the letter 'Н').

[1] Provided that the alloy contains not more than 3% Mg.

The values of ultimate strength and elongation of АМц alloys in various states are as follows:

Alloy state	М	П	Н
σ_t, kgf/mm²	13	16	22
δ, %	23	10	5

Manganese (in an amount up to 1%) is added to duralumins and other aluminium alloys mainly in order to increase their corrosion resistance.

26.7. DURALUMIN AND OTHER AGE-HARDENING DEFORMABLE ALLOYS

Duralumin[1] is the most popular among the aluminium alloys which are employed in deformed state and can be strengthened by heat treatment. It contains on the average 4% Cu, 0.5% Mn, and also magnium and iron.

Duralumin is an alloy of at least six components: aluminium, copper, magnesium, manganese, silicon, and iron, but only copper and magnesium are the principal alloying elements. For that reason, duralumins may be assumed to belong to the Al-Cu-Mg system. Silicon and iron are permanent impurities in duralumins and their presence is due to the use of insufficiently clean aluminium.

The alloying elements in duralumins can form a number of soluble compounds (which can cause ageing), such as $CuAl_2$, *S*-phase, Mg_2Si, and also insoluble compounds, for instance those of iron and manganese.

The structure of duralumin as annealed (Fig. 26.19*a*) consists of the solid solution and secondary inclusions of various intermetallics.

Upon hardening from the optimum temperature (500°C), the major quantity of $CuAl_2$ and Mg_2Si dissolves in aluminium, but iron compounds remain undissolved. Thus, the structure of an as-hardened alloy is the solid solution + inclusions of insoluble iron compounds (are shown black in Fig. 26.19).

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[1] Duralumin is the oldest aluminium-base alloy. It was invented by A. Wilm, a German metallurgist, in 1909 and was given its name after the Durener Metallwerke at Duren, in which Wilm worked. When experimenting with duralumin, Wilm discovered occasionally the phenomenon of natural ageing.

Important studies on the heat treatment of aluminium alloys were made in 1920's and 1930's and by P. Merica and M. Geiler.

In the USSR, the manufacture of duralumin was started in 1924 at the Kolchugino works (the alloy also contained 0.5% Ni and was named *kolchugaluminy*).

The nature of duralumin alloys, the effect of alloying elements, and heat treatment were studied in detail by various metallurgists (A. A. Bochvar, S. M. Voronov, Yu. G. Muzalevsky, D. A. Petrov, A. Guinier, G. D. Preston, I. N. Fridlander, V. A. Livanov, et al.).

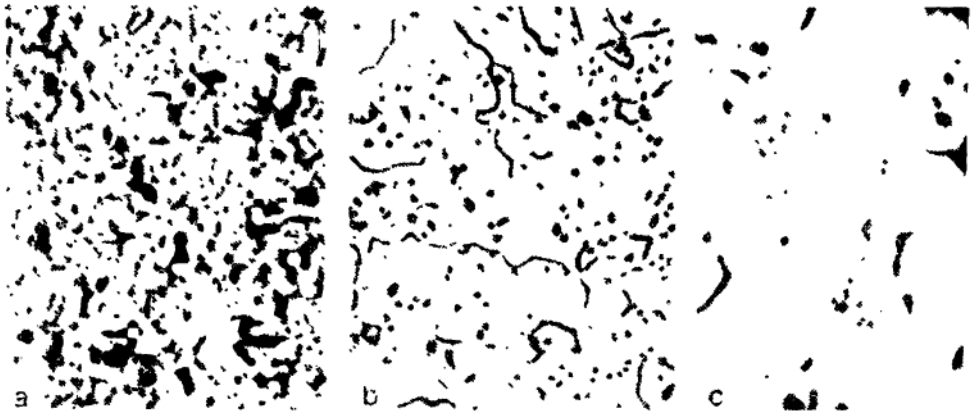

Fig. 26.19. Microstructures of duralumin
(*a*) as annealed. ×200; (*b*) as hardened. ×100; (*c*) overheated in hardening. ×200

During heating above 500-520°C, metal grains are fused on their boundaries and during cooling the portions of the liquid phase form a eutectic (Fig. 26.19*c*).

The mechanical properties of duralumin after the final heat treatment (hardening + ageing) depend appreciably on the temperature of hardening (Fig. 26.20). With an increase of the hardening temperature, intermetallic inclusions are dissolved, so that a more supersaturated solid solution forms on hardening and a higher strength is obtained on ageing. Heating above a certain limit causes overheating (grain coarsening and oxidation and fusion of grain boundaries), which results in a catastrophic loss of strength and plasticity. It is then clear that heat treatment of duralumin should be done with strict observance of the specified temperatures; temperature deviations should be not more than ±3-4°C. The hardening temperatures for various grades of duralumin will be given later in the book.

The ageing curves for duralumins have been shown in Fig. 26.8. Duralumins belong to naturally ageing aluminium alloys and the highest mechanical properties in normal duralumin are obtained during ageing at room temperature for five to seven days.

The heat treatment of these alloys consists in hardening from approximately 500°C with water quenching and subsequent natural (zone)

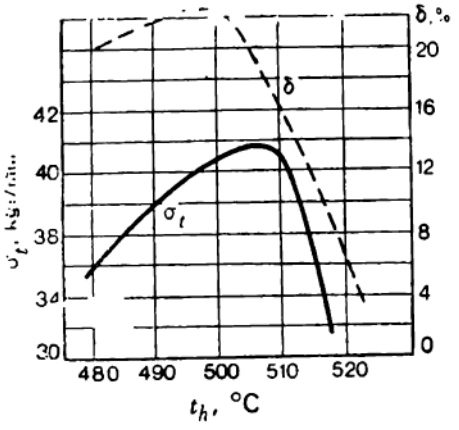

Fig. 26.20. Effect of hardening temperature on the mechanical properties of hardened and aged duralumin

ageing, i.e. parts made of these alloys are ready for use only in five-seven days after hardening.

Since duralumins have a low corrosion resistance, various methods have been searched for to protect them from corrosion. The most popular method is plating with pure aluminium[1]. Plated duralumin has the same corrosion resistance as pure aluminium.

The thickness of aluminium plating should be 4-8 per cent of the thickness of duralumin sheet (or of the diameter of wire or rod). Naturally, the layer of a less strong pure aluminium diminishes the total strength of the plated semi-product, i.e. plated duralumin is slightly less strong than unplated.

The compositions of various grades of duralumin are given in Table 26.5.

Table 26.5. Compositions of Duralumins, %% (GOST 4784—74)

Grade	Cu	Mn	Mg	Si	Fe
Д1	3.8-4.8	0.4-0.8	0.4-0.8	<0.7	<0.7
Д16	3.8-4.5	0.3-0.9	1.2-1.8	<0.5	<0.5

Alloy Grade Д1 is often called normal duralumin; the strengthening phase in it is formed by $CuAl_2$ compound*. Alloy Grade Д16, so-called *superduralumin*, is higher in magnesium than the normal grade. The main strengthening phase in Д16 is the *S*-phase which gives a higher strength than in Д1 alloy.

Table 26.6 gives the mechanical properties of these alloys in various states.

Table 26.6. Mechanical Properties of Duralumins

Grade	State, semiproduct	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %
Д1	As annealed	21	11	18
	As hardened and aged:			
	in rods	49	32	14
	in sheets	41	24	20
Д16	As annealed	22	11	18
	As hardened and aged:			
	in rods	54	40	11
	in sheets	44	33	18

[1] Plated duralumin is a typical bimetal (duralumin + aluminium).

* The presence and content of Mg_2Si compound is determined by the contamination of an alloy in silicon.

The heat treatment conditions for these alloys are as follows: hardening from 495-505°C for Д1 and from 490-500°C for Д16 (water quenching), ageing at 20°C for four days. Softening annealing is carried out at 340-370°C.

The physical properties of these alloys on heat treatment are practically the same:

Linear expansion	23×10^{-6}
Heat conductivity:	
as annealed	0.28
as hardened and aged	0.41
Electric conductivity (per cent to copper):	
as annealed	50
as hardened and aged	30
Modulus of elasticity, kgf/mm²	7 000
Poisson's ratio	0.31
Density, g/cm³	2.8

As can be seen from Table 26.6, pressed sections have a higher strength than sheets (for the same heat treatment conditions). This is explained by what is called the *extrusion effect*, i.e. the strain-hardening effect produced by pressing is not eliminated by heating for hardening. Evidently, the strengthening due to the extrusion effect is nothing more than that due to mechanical heat treatment (strain-hardening + hardening + ageing).

Despite the relatively low strength (σ_t = 40-50 kgf/mm²), aluminium alloys have an appreciably lower fracture toughness (K_{1c}) than steels (120-140 kgf/mm$^{3/2}$ against 500 kgf/mm$^{3/2}$ of a steel of the same strength; a value of $K_{1c} \cong$ 150-200 kgf/mm$^{3/2}$ is typical of a high-strength steel with $\sigma_t > 200$ kgf/mm²). This indicates that duralumins have a substantially lower (by a factor of 5) structural strength than steels.

It should also be noted that welding or soldering of aluminium alloys cannot produce a joint of the same strength as that of the main metal. A reliable method of connecting duralumin parts is riveting, with rivets being also made of duralumin. The metal of rivets should have an appropriate plasticity to allow good driving. Such properties are offered by duralumin in as-hardened state (before ageing).

Rivets made of alloys Д1 or Д16 should be driven in place not later than in two hours (Д1) or 20 minutes (Д16) after the hardening, i.e. when no noticeable ageing has occurred. If driven at a later time, cracking is possible in the rivet metal owing to the ageing and the loss of plasticity.

Naturally, such a strict requirement is difficult to be met. To avoid this, a special duralumin alloy (Д18) has been developed for rivets, which can be driven in as-aged state. The alloy has reduced contents of alloying elements (copper and magnesium) and has upon hardening and ageing an appreciably lower strength and a higher plasticity than, for instance, Д1 alloy.

The composition of Д18 alloy is 2.2-3% Cu and 0.2-0.5% Mg and its mechanical properties on water quenching from 495-505°C and natural ageing are as follows: σ_t = 30 kgf/mm², δ = 24 per cent, ψ = 50 per cent, and shear resistance[1] τ_{sh} = 19 kgf/mm².

As can be seen from Table 26.6, the ultimate strength of normal duralumin in sheets is only 41 kgf/mm² and that of the high-strength grade, 44 kgf/mm².

A higher strength is obtained in aluminium alloys which in addition to the main components, copper and magnesium, are alloyed with zinc, i.e. in alloys of the Al-Cu-Mg-Zn system*.

[1] The most important characteristic for rivets.

* These alloys are not actually duralumins since the latter belong to the Al-Cu-Mg system.

The strength of an Al + 10% Zn + 2% Mg alloy is as high as 60 kgf/mm², but drops appreciably even in weak corrosive media, such as distilled water. This drawback can be eliminated by alloying with approximately 2% Cu. A small addition of chromium or zirconium gives the same effect. Thus, quarternary Al-Zn-Mg-Cu alloys have come into use, the most typical in the system being B95 alloy (5-7% Zn, 1.8-2.8% Mg, 1.4-2% Cu, and 0.1-0.25% Cr), see Table 26.7. The strengthening effect in the alloy is mainly due to the dissolution of *T*-phase ($Al_2Mg_3Zn_3$).

Table 26.7. Mechanical Properties (Typical) of High-strength Aluminium Alloys of Al-Mg-Zn-Cu System

Alloy Grade	Semiproduct	Age-hardening conditions on hardening from 465°C	Mechanical properties		
			σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %
B95	Sheets	120°C, 2 h	52	44	12
	Rolled sections	140°C, 6 h	60	55	8
B96	Rolled sections	140°C, 6 h	68	64	7

Owing to the heavy alloying, the alloy has a lower melting point, so that the temperature for hardening is lower (460-470°C) compared to that for duralumin. The lower rate of decomposition of the supersaturated solid solution in B95 alloy (see Fig. 26.5) necessitates the following changes in the heat treatment conditions:

A. The rate of quenching can be reduced, which is effective for reducing internal stresses. A drawback inherent in high-strength aluminium alloys is that high internal stresses formed by hardening can make them susceptible to corrosion cracking. This is why B95 alloy is quenched in hot water (heated to 80-100°C), rather than in cold water.

Good results have been obtained by quenching alloys of this type in liquid nitrogen[1] which gives a lower quenching rate than in cold water (owing to the lower latent heat of vaporization of liquid nitrogen) and a more uniform cooling than in hot water.

B. Natural ageing of the alloy cannot ensure the maximum strength, even on a very long holding time. The maximum strength is obtained on artificial ageing for 16-24 h at 120-140°C.

If a high strength is essential, it is advisable to use a more heavily alloyed metal than B95 alloy.

The highest strength among aluminium alloys is shown by Grade B96 which contains 8-9% Zn, 2.3-3% Mg, 2-2.6% Cu, and 0.1-0.2% Zr. The ultimate strength of this alloy attains 68 kgf/mm². The mechanical properties of Al-Zn-Mg-Cu alloys are given in Table 26.7.

It should be noted however that it is not always reasonable to pursue after the highest strength, as this may be associated with a loss in toughness (for instance, K_{1c}), resistance to stress-induced corrosion, and in general with a loss of structural strength which is defined as the reliability of the material. In that connection, there is a trend to restrict the strength to a moderate value (of an order of 40 kgf/mm² for duralumins) so as to have a technologically favourable and reliable material; this is achieved by lowering the sum of zinc and magnesium

[1] Not to be confused with sub-zero treatment.

to not more than 6-6.5 per cent. An example is Grade 1915 alloy which contains on the average 3.7% Zn, 1.5% Mn, and 0.18% Zr.

In the group of lithium-containing alloys, let us discuss alloys of the types ВАД23 (1.2% Li, 5.3% Cu, and 0.15% Cd) and 01420 (5.5% Mg, 2.1% Li, and 0.12% Zr).

The strengthening heat treatment consists in hardening from 515-525°C (ВАД23) or 495-505°C (01420) with quenching in cold water and ageing at 170°C for 10-12 h, which ensures the maximum strength (σ_t = 55-60 kgf/mm²), but insufficient values of plasticity (δ = 4-5%) and structural strength (reliability).

Underageing (ageing at 160°C) or overageing (ageing at 200°C) gives a lower strength, but improves the plasticity.

Alloy Grade 01420 is the lightest among aluminium alloys; its density is 2.5 g/cm³, i.e. lower than that of pure aluminium (2.7 g/cm³) or of B95 alloy (2.9 g/cm³); this is essential for materials used in aircraft engineering.

26.8. ALUMINIUM ALLOYS FOR FORGINGS AND STAMPINGS

Many parts (for instance, propeller blades) are made from aluminium alloys by forging. An alloy for the purpose should have a high plasticity in hot state in addition to high mechanical properties. Forged parts are usually made of common duralumin[1] or other alloys of a similar composition (АК6, АК8).

The compositions of these alloys are given in Table 26.8 and their mechanical properties, in Table 26.9.

Table 26.8. Compositions of АК Alloys, %

Alloy Grade	Cu	Mg	Mn	Si	Fe
АК1	3.8-4.8	0.4-0.8	0.4-0.8	<0.7	<0.7
АК6	1.8-2.6	0.4-0.8	0.4-0.8	0.7-1.2	<0.6
АК8	3.9-4.8	0.4-1.0	0.4-1.0	0.6-1.2	<1.0
АК4*	1.9-2.5	1.4-1.8	0.15-0.35	0.5-1.2	1.1-1.6

* Also contains 1.0-1.5% Ni.

Table 26.9. Mechanical Properties of АК Alloys

Alloy Grade	Heat treatment	σ_t, kgf/mm²	δ, %
АК1	Hardening + natural ageing	38	10
АК6	Hardening + artificial ageing	36	7
АК8	Ditto	46	10

[1] Duralumin in forged or stamped state is graded as АК1.

The properties of these grades are somewhat worse than those of duralumin[1], because duralumin in sheets, tubes and other rolled sections has a finer structure than in forgings. The behaviour of these alloys in heat treatment does not practically differ from that of duralumin, as has been noted earlier.

A coarser structure of the second phase in АК alloys requires a longer holding time at the hardening temperature. Alloys of this group usually acquire better properties on artificial ageing.

26.9. SILUMINS AND OTHER ALUMINIUM ALLOYS FOR SHAPED CASTINGS

The group of aluminium alloys high in silicon is called *silumins*. Silumins are the most popular casting aluminium alloys and are used only in a cast state (for instance, in automotive and aircraft construction). Aluminium alloys with copper, magnesium and zinc are also used as casting alloys, but less frequently than silumins.

In order to obtain dense castings, use should be made of alloys having a narrow temperature interval of crystallization (see Fig. 26.17); naturally, alloys of the eutectic composition are best suitable for the purpose.

Many alloys of the eutectic composition in the systems Al-Cu, Al-Mg, etc. have very poor mechanical properties and are utterly unsuitable as casting alloys. An exception is the Al-Si system in which the eutectic is rather low in silicon[2] and the mechanical properties of eutectic alloys of this system turn out to be quite high (especially upon modifying). In view of this favourable combination of casting and mechanical properties, silumins have found a wide application.

The achievements in the application of casting aluminium alloys have been favoured by a number of circumstances. Casting technology has advanced much in the recent years. Casting of parts of an intricate shape and large size is now quite feasible. Many parts are precision-cast, often without allowances for machining[3]. The density of cast metal is now close to that in deformed state, which is achieved by carrying out the crystallization under pressure and by other technological improvements.

The mechanical properties of aluminium alloys in castings can be improved substantially by heat treatment. The ultimate strength and elongation of casting aluminium alloys can be increased by heat treatment (hardening + + artificial ageing) by a factor of two.

Heat treatment of casting aluminium alloys has certain specifics compared to heat treatment of deformed alloys, which may be explained by the differences in the composition and structure (casting alloys have a coarser structure).

Casting alloys should be heated for hardening to a higher temperature and held at that temperature for a longer time. This is dictated by the need to dis-

[1] As may be seen by comparing alloys of a similar composition such as Grade Д1 and АК1 in Tables 26.6 and 26.8.

[2] 11.7% Si, whereas the eutectic in the Al-Cu system has 33% Cu and that in the Al-Mg system, 34.5% Mg.

[3] Precision casting, permanent-mould casting, shell casting, and pressure die-casting.

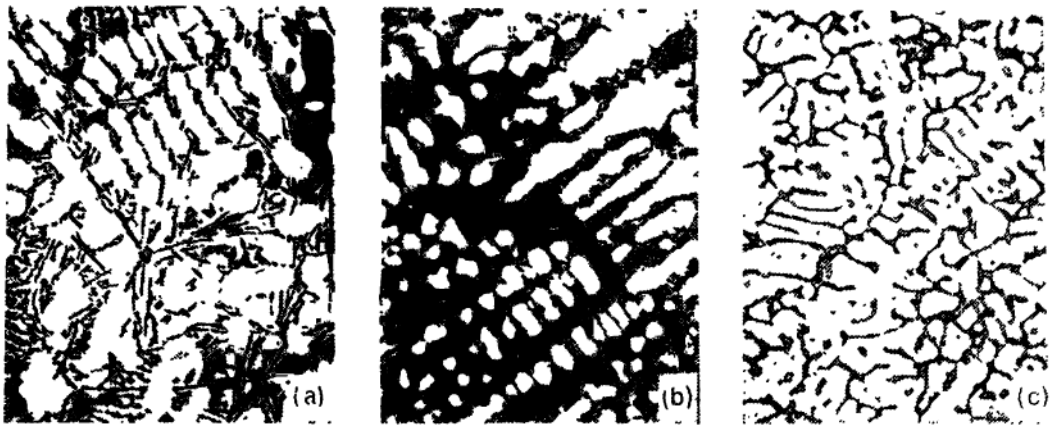

Fig. 26.21. Microstructures of casting aluminium alloys. ×200
(*a*) unmodified silumin; (*b*) modified silumin; (c) typical structure of a casting aluminium alloy (Al + 12% Cu)

solve coarse intermetallic inclusions, which are usually located on the grain boundaries, and to equalize the concentration over the volume of grains.

Casting alloys are almost insusceptible to natural ageing and the maximum strength can be obtained in them by artificial ageing for 10-20 h at 150-180°C[1].

As with deformed alloys, the strengthening effect in casting alloys is explained by the dissolution of intermetallic compounds $CuAl_2$, Mg_2Si, *S*-phase, Al_3Mg_2, etc., with a supersaturated solid solution being formed in as-hardened state. An increase in both the strength and toughness upon heat treatment may be due to the dissolution of the indicated intermetallic compounds, which have been present in the cast state on the grain boundaries. This is why the mechanical properties can in some cases be improved solely by hardening. Ageing usually increases the strength even more, but lowers the plasticity.

Binary aluminium-silicon alloys and in general all high-silicon alloys can be only slightly strengthened by hardening and ageing[2], but their mechanical properties can be improved substantially by a special treatment in the liquid state. Common silumin contains 12-13% Si and is a typical hypereutectic alloy in its structure which consists of coarse-grained acicular Al + Si eutectic and primary silicon inclusions (Fig. 26.21*a*). If however a small quantity of sodium or another substance (such as 2/3 NaF + 1/3NaCl) is added to the melt just before casting, the structure of the cast metal will change sharply. It will now be a hypoeutectic alloy with the structure consisting of bright precipitates of primary aluminium and a fine-grained eutectic (see Fig. 26.21 *b*). The process is called *modification*.

A modifier added in the amount up to 1 per cent of the mass of the melt inhibits crystallization of silicon, and therefore, silicon will

[1] Or at a higher temperature and for a shorter time.
[2] This is not always true of casting aluminium alloys of a more complex composition.

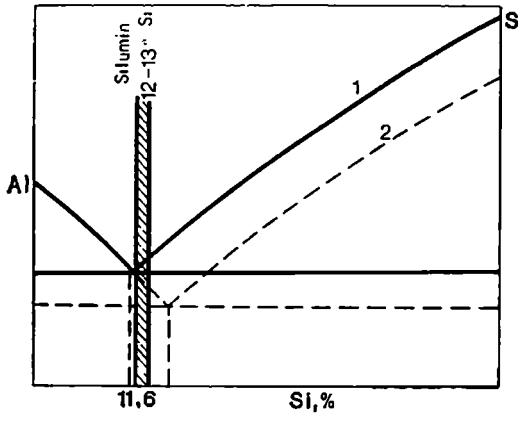

Fig. 26.22. Effect of modification on crystallization in Al-Si system (schematic)

1 — without modification; *2* — upon modification

precipitate and the eutectic will crystallize at a lower temperature (Fig. 26.22) and into a finer structure. As shown in Fig. 26.22, a hypereutectic alloy with 12-13% Si can be made hypoeutectic by lowering the line of the beginning of silicon crystallization and the temperature of crystallization of the eutectic.

The mechanical properties in a modified alloy are improved owing to the refinement of the structure and the absence of primary precipitates of brittle silicon. For instance, an alloy with 13% Si has $\sigma_t = 14$ kgf/mm^2 and $\delta = 3$ per cent before modification and $\sigma_t = 18$ kgf/mm^2 and $\delta = 8$ per cent in the modified state.

Despite their excellent casting properties, binary aluminium-silicon alloys cannot always satisfy the high requirements on the mechanical properties. Al-Si alloys with 13% Si (Grade АЛ2) are used for casting intricate-shape parts of which high mechanical properties are not needed. At more rigorous requirements on the strength properties, use is made of a special type of silumin—hypoeutectic silumins with 4-10% Si and additions of copper, magnesium and manganese (Grades АЛ3, АЛ4, АЛ5, АЛ6, АЛ9).

The mechanical properties of special silumins upon heat treatment are as follows: $\sigma_t = 20$-25 kgf/mm^2 and $\delta = 1$-6 per cent, i.e. are substantially lower than in deformed alloys, which is due to a coarser structure (not refined by plastic deformation), see Fig. 26.21*a*.

Among casting alloys, the highest mechanical and corrosion-resisting properties are shown by Grade АЛ8, an aluminium-magnesium alloy with 9.5-11.5% Mg. On being heat treated it can have an ultimate strength of 30 kgf/mm^2 at an elongation of 12 per cent. The alloy has however poorer casting properties than other alloys in the group.

The use of casting alloys for stressed parts is reasonable only in cases when a cast part can have an appreciably lower mass than that made by forging or when the given shape cannot be formed by forging; in all other cases, forging alloys, which have a higher mechanical strength, should be preferred.

The compositions of selected grades of casting alloys are given in Table 26.10. In the grading of these alloys, A stands for aluminium, Л for casting, and a digit is the serial number in the State Standard GOST.

As has been noted, АЛ2 is a normal silumin, Grades АЛ4 and АЛ9 have a reduced content of silicon and additions of magnesium and manganese to improve their mechanical properties.

Table 26.10. Compositions of Casting Aluminium Alloys

Alloy Grade	Main constituents				Impurities[1] (maximum)	
	Mg	Si	Mn	Cu	Fe	Total
АЛ2	—	10-13	—	—	0.8-1.5	2.2-2.8
АЛ4	0.17-0.30	8.0-10.5	0.25-0.50	—	0.6-1.2	1.1-1.7
АЛ9	0.2-0.4	6.0-8.0	—	—	0.3-1.0	1.0-1.9
АЛ3	0.2-0.8	4.0-6.0	0.2-0.8	1.5-3.5	1.0-1.5	1.3-1.8
АЛ5	0.35-0.60	4.5-5.5	—	1.0-1.5	0.6-1.5	1.0-1.7
АЛ6	—	4.5-6.0	—	2.0-3.0	1.1-1.4	1.8-2.0
АЛ11*	0.1-0.3	6.0-8.0	—	—	0.8-1.2	1.8-2.0
АЛ7	—	—	—	4-5	<1.0	<2.2
АЛ12	—	—	—	9-11	1.0-1.2	2.8-3.0
АЛ8	9.2-11.5	—	—	—	<0.3	<1.1

[1] The maximum content of impurities depends on the casting process; pressure die casting allows a higher content of iron than sand casting.
* Also contains 10-14% Zn.

Grades АЛ3, АЛ5 and АЛ6 are low-silicon silumins additionally alloyed with copper (and also with small amounts of magnesium and manganese); they possess poorer casting and better mechanical properties. Grade АЛ11 is a zinc-alloyed silumin; the heavy alloying with zinc improves the casting properties. The alloy is used for making especially complicated castings.

The last three grades in Table 26.10 contain no silicon and are not actually silumins.

The Al-Cu alloys Grades АЛ12 and АЛ7 differ substantially from each other. Grade АЛ7, which contains 4-5% Cu, is close in its composition to duralumin and has high mechanical and poor casting properties. It is used to cast small parts to be subjected to appreciable mechanical actions. On the contrary, Grade АЛ12 has good casting and low mechanical properties, is inferior in this respect to normal silumin and cannot be recommended for application (Grade АЛ12 is the oldest in the group of casting aluminium alloys).

Finally, Grade АЛ8 represents the group of *magnalium* alloys, i.e. alloys of the Al-Mg system. It has a high mechanical strength, which is however lower than in other casting aluminium alloys, a high density, high corrosion resistance, but is inferior in casting properties to the other alloys (it is clear if we consider the position of this alloy in the Al-Mg constitutional diagram, Fig. 26.13).

Table 26.11 gives the typical mechanical properties of selected casting alloys (as measured on cast specimens)[1].

The wide assortment of casting alloys makes it possible to choose an optimal grade for every particular application according to the mechanical, casting and other properties of a particular grade.

[1] Specimens cut from a cast part usually show lower mechanical properties.

Table 26.11. Mechanical Properties of Casting Aluminium Alloys

Alloy Grade	Casting process	Heat treatment	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %	*HB*	Density, g/cm³
AJI2	Sand c.	—	18	8	7	50	2.66
	Chill c.	—	22	9	5	55	—
AJI4	Sand c.	Hardening+ ageing	26	20	4	60	2.65
AJI9	Sand c.	Hardening+ ageing	20	11	6	75	2.68
AJI6	Sand c.	Ditto	24	14	4	80	2.76
AJI7	Sand c.	Ditto	28	21	2	95	2.81
AJI12	Sand c.	Ditto	20	12	1	—	2.91
AJI18	Sand c.	Hardening	30	17	12	75	2.58
	Chill c.	Ditto	33	18	15	80	—

26.10. HEAT-RESISTING ALUMINIUM ALLOYS

A group of special aluminium alloys with additions of copper, magnesium, nickel, iron, and titanium are used for making (by casting or die-forging) various machine parts (such as cylinder head and pistons of internal combustion engines and the like) for operation at elevated temperatures of an order of 200-300°C or even 350°C.

The required properties in these alloys are formed by hardening (which transfers the excess phases into the solid solution) and artificial ageing (to stabilize the structural state).

With a more complicated composition of an alloy and its excess phases, the softening at elevated temperatures occurs more slowly. This is why heat-resisting aluminium alloys usually have a complex composition with special additions of iron and nickel[1] and in that respect differ widely from other aluminium alloys.

The compositions of Soviet-made heat-resisting aluminium alloys for aircraft construction are given in Table 26.12.

Table 26.12. Compositions of Heat-resisting Aluminium Alloys, %

Alloy Grade	Cu	Mg	Mn	Ni	Fe	Si
AK2	3.5-4.5	0.4-0.7	< 0.2	1.8-2.3	0.5-1.0	< 0.8
AK4	1.9-2.5	1.4-1.8	< 0.2	1.0-1.5	1.1-1.6	< 0.8

Note. Both alloys contain 0.05-0.12% Ti.

[1] The purpose of iron and nickel is evidently to slow down the diffusion processes which cause softening of an alloy at high temperatures.

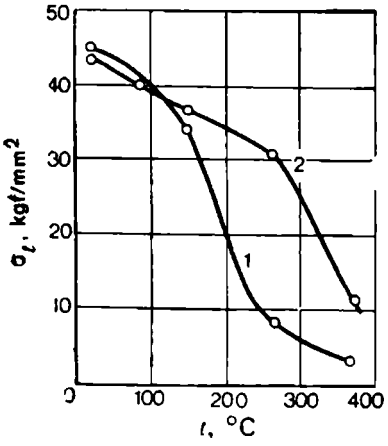

Fig. 26.23. Ultimate strength of (*1*) АК2 and (*2*) АК4 alloy at elevated temperatures

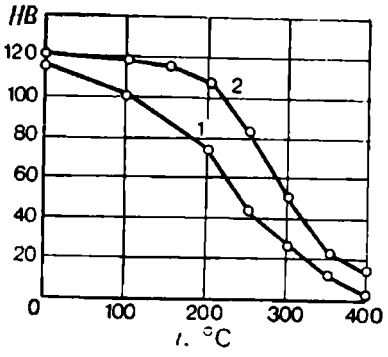

Fig. 26.24. Hardness of (*1*) Д1 and (*2*) АК4 alloy at elevated temperatures

Figure 26.23 shows the effect of test temperature on the strength level of these alloys (АК2 and АК4) and Fig. 26.24, the hardness of duralumin and heat-resisting АК4 alloy at elevated temperatures. As may be seen from the latter figure, alloy АК4 has certain advantages over Д1 duralumin, which has a simpler composition, especially in the temperature range of 150-300°C. At temperatures above 350-400°C there is however no noticeable difference in the properties of these two alloys.

Heat treatment of heat-resisting forging alloys (АК2, АК4) consists in hardening from 510-520°C and artificial ageing at 100-180°C for 15-20 h.

Alloys for making pistons should have a high heat conductivity and low values of density and the coefficient of friction. АК2 and АК4 alloys have a density of 2.80 g/cm³ and their coefficient of linear expansion at 20-400°C is 22; their heat conductivity is respectively 1.55 and 1.68 J/(cm s °C).

An example of casting heat-resisting aluminium alloys is Grade АЛ1 which contains 3.75-4.50% Cu, 1.25-1.75% Mg, 1.75-2.25% Ni, <0.8% Fe, <0.7% Si, and <0.3% Zn. Its heat resistance is due to the formation of a rigid network of Mg_2Si and $Al_xCu_y(Fe, Ni)_z$ compounds during crystallization.

The mechanical properties of heat-resisting aluminium alloys are given in Table 26.13.

Table 26.13. Mechanical Properties of Heat-resisting Aluminium Alloys at Elevated Temperatures

Alloy Grade	σ_t, kgf/mm², at temperature, °C				δ, at temperature, °C			
	20	150	260	315	20	150	260	315
АЛ2	28	26	10	6	0	1	10	30
АК2	44	34	8	5	17	10	32	50
АК4	43	36	31	15	18	20	15	20

As may be seen, the casting АЛ2 alloy has a higher strength at elevated temperatures and a lower plasticity compared to the forging АК2 alloy; Grade АК4 excels the two former alloys in its properties.

MAGNESIUM, BERYLLIUM AND THEIR ALLOYS

26.11. MAGNESIUM

Like aluminium, magnesium was discovered by H. Davy in 1808. Metallurgical problems of making pure magnesium were solved in 1930's and 20 tons of magnesium were manufactured industrially in 1937. In 1943, the world production of magnesium (without the USSR) rose to 250 000 t.

Magnesium has the lowest density among all commercial metals (1.7 g/cm^3), which predetermined its wide use in various branches of industry, in the first place in aircraft engineering where low density is a valuable property. Magnesium crystallizes into a hexagonal lattice ($a = 3.2$ Å, $c = 5.2$ Å) and has no allotropic modifications. Its melting point is low (651°C). For other physical properties of magnesium see Table 26.1.

Magnesium and its alloys are poorly corrosion resistant. Pure magnesium is relatively stable only in dry atmospheric air. With increasing temperature it begins to oxidize intensively and can even ignite. This requires special safety measures to prevent oxidation and ignition of liquid magnesium during casting.

Unlike Al_2O_3 film on aluminium, MgO film on magnesium has no protective properties; it has an appreciably higher density (3.2 g/cm^3) than magnesium and for that reason cracks easily. The rate of oxidation of magnesium increases rapidly with temperature and at temperatures above 500°C magnesium ignites and burns, forming a dazzling bright flame.

Magnesium has low values of strength and plasticity. Its low plasticity is due to the small number of preferable slip planes in the hexagonal lattice. Rolled and annealed magnesium has on the average the following properties: $\sigma_t = 18$ kgf/mm^2, $\sigma_{0.2} = 10$ kgf/mm^2, $\delta = 15$ per cent, hardness 30 *HB*. Because of these low values, pure magnesium cannot be used as a structural material. Commercial magnesium can be used in pyrotechnics, in chemical technology, and as deoxidant and modifier. Its ultimate strength can however be raised to 30-35 kgf/mm^2 by proper alloying and heat treatment, and therefore, magnesium alloys can be used for engineering purposes owing to their favourable strength-to-density ratio.

26.12. MAGNESIUM ALLOYS

The principal additions in magnesium alloys are aluminium, zinc, and manganese which are soluble in magnesium (Fig. 26.25). Their solubility diminishes as the temperature is lowered, which makes it possible to employ heat treatment (hardening + ageing).

It should be noted that heat treatment is not so essential for magnesium alloys as for aluminium alloys, since it does not change appreciably their properties.

Apart from aluminium, zinc and manganese which are permanent components of commercial magnesium alloys[1], some other elements can also be added, usually in quantities of a few hundredths of a per cent[2].

Like aluminium alloys, magnesium alloys are divided into deformable and casting grades (the former are graded as MA and the latter, as MЛ).

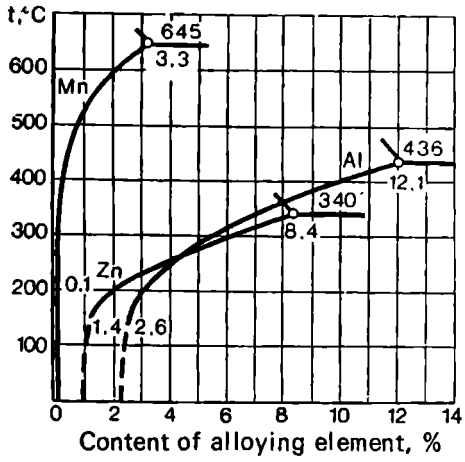

Fig. 26.25. Solid solution regions in Mg-Mn, Mg-Al and Mg-Zn systems

The compositions of the most common deformable magnesium alloys are given in Table 26.14 and their mechanical properties, in Table 26.15.

Table 26.14. Compositions (%) of Deformable Magnesium Alloys (GOST 14957—69)

Alloy Grade	System	Al	Zn	Mn	Other elements
MA1	Mg-Mn	—	—	1.3-2.5	—
MA2	Mg-Al-Zn	3-4	0.2-0.8	0.15-0.50	—
MA5	Mg-Al-Zn	7.8-9.2	0.2-0.8	0.15-0.5	—
MA10	Mg-Al-Cd-Ag	7.8-8.8	—	0.2-0.6	7-8 Cd; 2-2.5 Ag
MA11	Mg-Nd-Mn	—	—	1.5-2.5	2.5-4.0 Nd, 0.1-0.25 Ni

The presence of manganese gives somewhat higher values of corrosion resistance and augments mechanical properties. Aluminium improves the strength properties more substantially than manganese (owing to the formation of solid solution), so that an alloy with 3-4% Al has an ultimate strength as high as 30 kgf/mm^2. Naturally, an alloy with 3-4% Al cannot be strengthened substantially by heat treatment; the same is true of MA1 alloy which contains no aluminium. On the other hand, alloy grades MA5 and MA10 which contain 8-9% Al, have an ultimate strength of the order of 40 kgf/mm^2 upon hardening (from 400°C) and ageing (at 175°C).

Note that the strengthening effect in magnesium alloys is not very pronounced ($\Delta\sigma_t$ = 3-4 kgf/mm^2, $\Delta\sigma_{0.2}$ = 5-8 kgf/mm^2) and often the heat

[1] Aluminium and zinc are usually added to produce the strengthening effect and manganese, to increase the corrosion resistance and refine the grain.

[2] For instance, zirconium and rare-earth metals can be added for grain refinement and beryllium, to diminish the ignition hazard in casting.

Table 26.15. Mechanical Properties (Typical) of Deformable Magnesium Alloys

Alloy Grade	State	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %	Alloy Grade	State	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %
MA1	Annealed	21	12	8	MA5	Annealed	32	22	14
MA2	Ditto	28	18	10	MA10	Hardened + aged	43	30	6

Note. The properties were tested on pressed rods.

treatment procedure is reduced to hardening which raises noticeably the plastic properties and slightly, the strength (owing to homogenization and dissolution of boundary precipitates). Alloy Grade MA10 has probably the highest strength among magnesium alloys ($\sigma_t > 43$ kgf/mm²) and the highest strength-to-density ratio.

It is interesting to compare the strength-to-density ratios for alloys based on various metals taking as examples the strongest alloys from each group:

Base metal	Magnesium	Aluminium	Titanium	Iron
Alloy . . .	MA10	B95	BT6	H18K9MA
σ_t/γ	$\frac{43}{1.8}=2.4$	$\frac{60}{2.9}=2.1$	$\frac{100}{4.5}=2.2$	$\frac{180}{7.8}=2.3$

As may be seen, the values of unit strength (strength-to-density ratio) coincide quite closely, i.e. these metals compete severely with one another in the unit strength.

Evidently, to make alloys of a base metal competitive to other metals, their strength should be raised (since it is impossible to lower the density appreciably) without any loss in plasticity and toughness (reliability). It may be expected that the following values of ultimate strength will be attained in various alloys in the near future: 50 kgf/mm² in magnesium alloys, 75 kgf/mm² in aluminium alloys, 130 kgf/mm² in titanium alloys and 220 kgf/mm² in iron alloys[1].

The compositions and mechanical properties of casting magnesium alloys are given in Tables 26.16 and 26.17.

[1] It is interesting to note that the strength-to-density ratio is numerically equal to the *length of fracture* in kilometres; i.e. a wire, say of steel H18K9MA, will break under its own weight at a length of 2.3 km; this is why unit strength is often measured in kilometres.

Table 26.16. Compositions (%) of Casting Magnesium Alloys (GOST 2856—68)

Alloy Grade	System	Al	Zn	Mn
MJI2	Mg-Mn	—	—	1-2
MJI3	Mg-Al-Zn	2.5-3.5	0.5-1.5	0.15-0.50
MJI4	Mg-Al-Zn	5-7	2-3	0.15-0.50
MJI5	Mg-Al-Zn	7.5-9.0	0.2-0.8	0.15-0.50
MJI6	Mg-Al-Zn	9-10.2	0.6-1.2	0.1-0.5
MJI10*	Mg-Nd-Zr	—	0.1-0.7	—
MJI12**	Mg-Zn-Zr	—	4-5	—

* Also contains 0.4-1% Zr and 2.2-2.8% Nd.
** Also contains 0.6-1.1% Zr.

Table 26.17. Mechanical Properties (Typical) of Casting Magnesium Alloys

Alloy Grade	State	σ_t, kgf/mm²	$\sigma_{0.2}$, kgf/mm²	δ, %
MJI2	Not heat-treated	12	3.5	4
MJI3	Ditto	18	5.5	8
MJI4	Ditto	18	9.5	5
	Hardened + aged	25	12	4
MJI5	Not heat-treated	16	11	1.5
	Hardened + aged	26	15	2
MJI10	Ditto	22	12.5	5
MJI12	Ditto	27	18	6

Casting magnesium alloys are close to deformable alloys in their composition, but have noticeably poorer mechanical properties, which is associated with a coarse structure formed by casting (Fig. 26.26). Heat treatment (homogenization during heating for hardening) can dissolve the excess phases concentrated at the grain boundaries and thus increase the plasticity and strength.

As may be seen, the level of strength attained in these alloys is 25-27 kgf/mm², with a low plasticity (δ = 2-4%).

The properties of magnesium alloys can be improved by using a clean charge (free from harmful impurities, such as iron), and by the addition of modifiers which form insoluble phases in the melt; these serve as crystallization nuclei and produce a finer grain on crystallization.

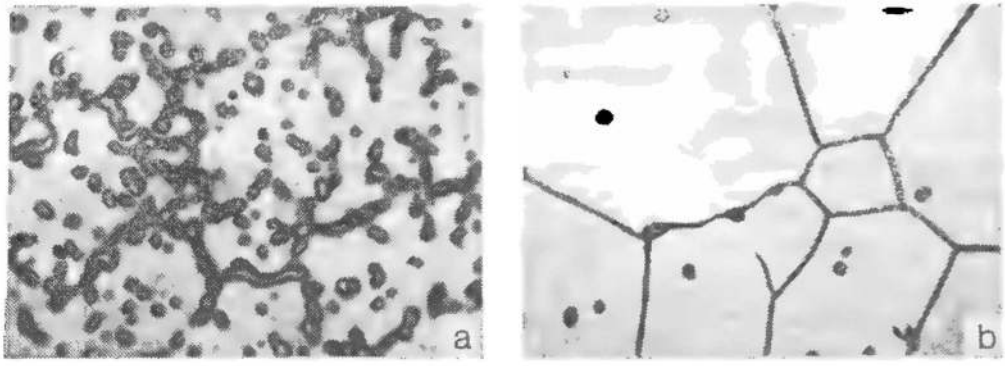

Fig. 26.26. Microstructures of MJI5 alloy, ×250
(*a*) as cast (α-solution + Mg_4Al_3 inclusions); (*b*) as hardened (supersaturated α-solution)

Magnesium alloys, both casting and deformable grades, can be used as heat-resisting alloys[1], in particular, Grade MA11 (deformable) and Grade MJI12 (casting) are suitable for the purpose.

26.13. BERYLLIUM

Some information on beryllium has been given in Ch. 25, on metals for nuclear engineering. Beryllium, however, belongs to light metals and can be used for the same purposes as the other light metals (aluminium or magnesium).

The element beryllium was discovered even earlier than aluminium or magnesium (in 1797 by L.N. Vauquelin) and first samples of metallic beryllium were obtained in 1827.

Beryllium has a high cost and will probably remain expensive in the future, which is due to its rare occurrence in the Earth's crust (only 0.0005% compared to 5.1% of Fe and 7.5% of Al). It can be expected therefore that beryllium and its alloys will be used only in exceptional cases where no appropriate substitute will be available for a particular special application.

Beryllium and especially beryllium alloys have a low density (1.8 g/cm³), high values of elastic modulus and strength, good dimensional stability, and a high corrosion resistance in various media.

Note that beryllium is toxic[2] and has a low plasticity. The last circumstance is due to its hexagonal lattice ($a = 2.3$ Å, $c = 3.6$ Å).

Some physical properties of beryllium are given in Table 26.1.

The mechanical properties of beryllium are roughly as follows: $\sigma_t = 25$ kgf/mm², $\delta = 1$ per cent. Extrusion of beryllium produces a textured structure in which the ultimate strength in the direction of deformation increases up to 70 kgf/mm² and the plasticity (δ), up to 10 per cent. This is indicative of a high anisotropy of properties which is equal at room temperature to 2 for the strength and to 10 for plasticity.

The curves of Fig. 26.27 illustrate the mechanical characteristics of beryllium (properties along and across the deformation axis, and also properties at various temperatures).

Beryllium is manufactured by metalloceramic technique (see Sec. 17.6) with hot plastic deformation after sintering. The size of powder particles affects the properties of the sintered beryllium. Finer particles produce a higher strength

[1] Up to 400°C for short-time and up to 250-300°C for long-time operation.
[2] When working with beryllium, especially with its dust and oxides, all safety and sanitary regulations should be strictly observed.

(for instance, σ_t = 40 kgf/mm² with a particle size of 10 μm and 50 kgf/mm², with 5 μm). The final product must retain its fine grain in order to have high mechanical properties.

Beryllium is annealed at 600°C to release internal stresses and subjected to recrystallization annealing at 800°C (it has an unusually high ratio $T_{recr}/T_{m.p.}$ = = 0.6).

It has been discovered quite recently that beryllium undergoes a polymorphic transformation (its second form, Be_β, has a cubic lattice and the temperature of $\alpha \rightleftarrows \beta$ transformation is 1 250°C). It may be expected in that connection that the properties of beryllium can be improved by heat treatment (structural recrystallization). The high-temperature β-phase is plastic but attempts to undercool it to room temperature by alloying or by quick cooling have been unsuccessful.

26.14. BERYLLIUM ALLOYS

Beryllium is an element with small atomic parameters. Since other elements have large parameters, alloying distorts substantially the crystal lattice of beryllium and decreases still more its low plasticity. The properties of beryllium are, as a rule, not improved by alloying: they are the better, the purer is beryllium. For instance, the presence of silicon in beryllium in an amount of only 0.001 per cent makes the metal utterly brittle.

An addition of oxygen improves the properties of beryllium (Fig. 26.28), whereas in all other metals oxygen is the most harmful impurity.

Despite these difficulties, attempts are being continued to develop beryllium-based alloys.

An alloy of Be + 4-5% Cu seems to be promising. The addition of copper diminishes the sharp anisotropy of beryllium and thus produces a positive effect. It may be expected that two-phase (Be + Be + Al-eutectic) alloys of beryllium with 20-35% Al will find a certain application; they have a higher density (some 2 g/cm³), but a higher plasticity than pure beryllium, probably owing to the presence of aluminium in the eutectic.

Beryllium is used industrially as an alloying element (for instance, in beryllium bronzes, Sec. 27.4) and in nuclear engineering; experiments are being carried out on using beryllium and its alloys in aircraft engineering and instrument-making.

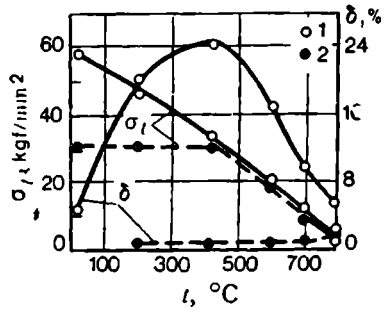

Fig. 26.27. Mechanical properties of beryllium (*1*) along and (*2*) across the rolling direction

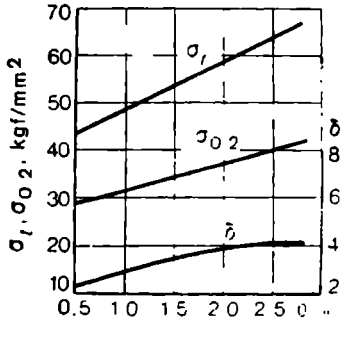

Fig. 26.28. Effect of oxygen on the mechanical properties of beryllium

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Chapter 27

COPPER AND COPPER ALLOYS

27.1. COPPER

Like gold and silver, copper occurs in virgin form in nature and the ancient Man was able to use copper long before he gained knowledge on metallurgy (i.e. on how to extract metals from their ores). At that time iron (of meteoritic origin) was valued much higher than copper or even gold, since its properties rendered iron more suitable for making weapons[1].

At present, copper is made by metallurgical techniques, i.e. by reducing it from oxides and sulphides in copper ores.

Though the content of copper in the Earth's crust is not high (0.01%), copper occurs in concentrated ore deposits where its content is rather high (of the order of 5%).

The production of copper increases gradually and at present copper is produced almost in the same amount as aluminium[2].

Table 27.1. Principal Physical Properties of Noble and Semi-noble Metals

Property	Cu	Ag	Au
Atomic number	29	47	79
Atomic mass	63.5	107.9	197.0
Density at 20°C, g/cm³	8.9	10.5	19.3
Melting point, °C	1 083	961	1 064
Boiling point, °C	2 595	2 530	2 212
Crystal lattice	f.c.c.	f.c.c.	f.c.c.
Lattice parameter at 20°C, Å	3.61	4.08	4.07
Coefficient of linear expansion, $\alpha \times 10^6$	16.5	14.2	9.7
Electric resistivity, ohm cm $\times 10^{-6}$	1.7	1.5	2.1
Normal elasticity modulus, kgf/mm	12 000	7 500	8 000

Copper is similar in its properties to silver and gold (Table 27.1), though gold and silver do not oxidize in air and are called noble metals, while copper oxidizes slightly and is called semi-noble.

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[1] At the time of the Troyan war, only kings could afford swords made of iron.

[2] The world production of copper (without the USSR) was 2.7 mln t in 1953, 3.8 mln t in 1960 and 6 mln t in 1966.

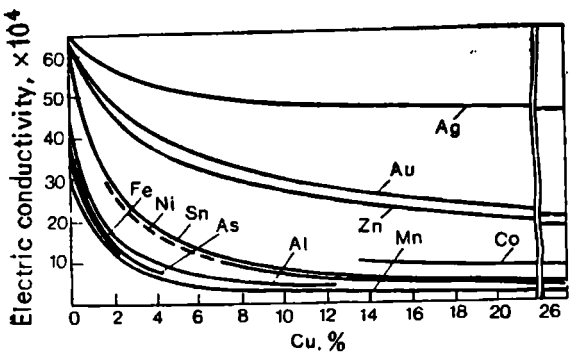


Fig. 27.1. Effect of impurities on the electric conductivity of copper

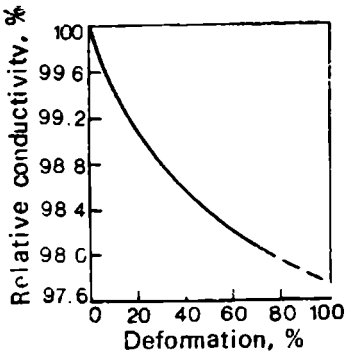


Fig. 27.2. Effect of work hardening on the electric conductivity of copper

Pure copper has a number of valuable properties (high plasticity, high electric and thermal conductivity, low oxidizability) because of which it has found a wide application. Besides, copper is the base in many important alloys, such as brasses and bronzes.

Owing to its high electric conductivity, copper has found a preferential application in electrical engineering. It is inferior only to silver in this characteristic. The values of electric resistivity for selected metals are as follows: 1.5×10^{-6} ohm cm for silver, 1.7×10^{-6} for copper, 2.7×10^{-6} for aluminium and 9.8×10^{-6} ohm cm for iron.

All impurities diminish the electric conductivity of copper, as may be seen from Fig. 27.1. The same effect is produced by strain hardening (Fig. 27.2). This is why annealled copper is used in wire conductors if a high strength is not essential; and only aerial wires, where a high tensile strength is required, are made of work-hardened copper or of copper alloys with small additions of active strengtheners (for instance, with 1% Cd).

The mechanical properties of pure copper are given in Table 27.2.

Table 27.2. Mechanical Properties of Pure Copper

State	σ_t, kgf/mm²	δ, %
As cast	15-20	15-25
Rolled and annealed	25-27	40-50
Strain-hardened	40-43	1-2

Copper of a rather high purity can be produced by electrolysis. Extra-pure copper contains 99.999% Cu, and is used in scientific research, but commercial common-purity copper contains 0.1-0.5 per cent of impurities (see Table 27.3).

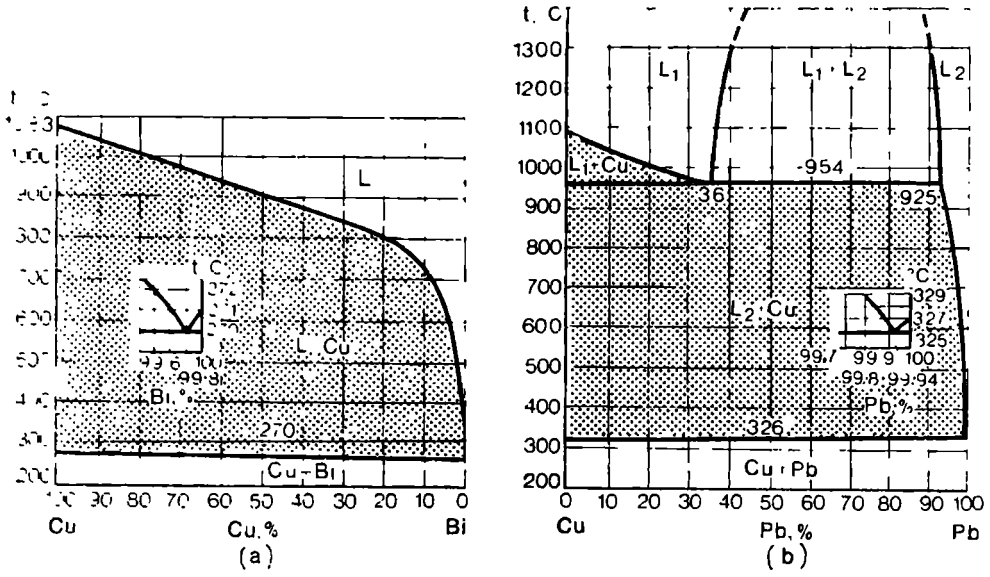


Fig. 27.3. Constitutional diagrams
(*a*) Cu-Bi; (*b*) Cu-Pb

The most harmful impurities in copper are bismuth and lead. They are almost insoluble in copper and form low-melting eutectics; the eutectic in the Cu-Bi system contains 99.8% Bi (Fig. 27.3*a*) and that in the Cu-Pb system, 99.94% Pb (Fig. 27.3*b*).

Table 27.3. Compositions (%) of Commercial Copper (GOST 859—66)

Grade	Cu	Impurities (maximum)			Grade	Cu	Impurities (maximum)		
		Bi	Pb	total			Bi	Pb	total
M000	99.99	0.0005	0.001	0.01	M2	99.7	0.002	0.01	0.3
M1	99.9	0.001	0.005	0.1	M3	99.5	0.003	0.05	0.5

The crystallization of Cu-Bi and Cu-Pb alloys actually comes to its end at the melting points of these metals (respectively at 270° and 327°C) and the

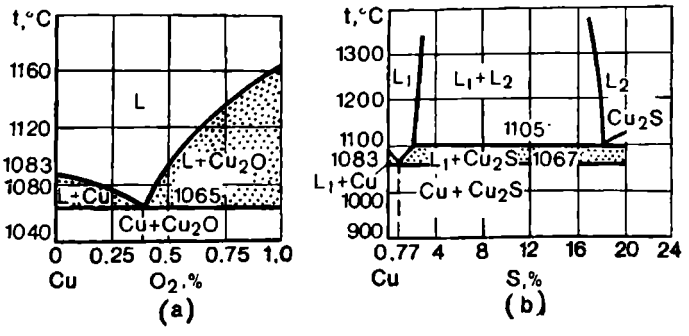


Fig. 27.4. Constitutional diagrams
(*a*) Cu-O_2; (*b*) Cu-S

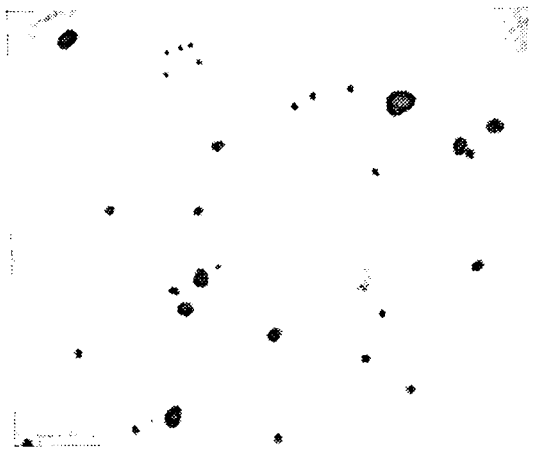


Fig. 27.5. Cu_2O inclusions in rolled copper

structure of a solidified alloy consists of copper crystals that have precipitated earlier and of shells of bismuth or lead which envelop them. Heating the alloy above the melting point of Bi (or Pb) disturbs the bonds between the primary copper crystals (causes red shortness). The alloy is very brittle and cannot be rolled. Even a few thousandths of a per cent of bismuth can make copper red-short; lead causes red-shortness when present in a concentration of a few hundredths of a per cent.

Sulphur and oxygen are also insoluble in copper, but the latter can form copper-rich eutectics with its oxide or sulphide, which contain 0.39% O_2 (Fig. 27.4*a*) or respectively 0.77% S (Fig. 27.4*b*) and melt at 1 065° or 1 067°C, i.e. well above the common temperatures of hot working of copper. This is why neither oxygen nor sulphur cause red shortness.

The Cu + Cu_2O eutectic in cast copper has a dotted structure and solidifies on the grain boundaries. It is destroyed by plastic working, so that oxygen is present in deformed copper in the form of separate Cu_2O inclusions (Fig. 27.5).

Oxygen-containing copper can suffer during heating from what is called the *hydrogen pest*. If copper is being heated in a hydrogen-rich medium (for instance, the products of incomplete combustion of fuel), hydrogen diffuses into copper and reduces copper oxide by the reaction $Cu_2O + H_2 = 2Cu + H_2O$. Water vapours that are formed produce a high pressure and therefore can cause cracking in metal discontinuities.

27.2. COPPER-ZINC ALLOYS (BRASSES)

Copper-zinc alloys for industrial applications can contain up to 45% Zn and are called *brasses*.

The Cu-Zn constitutional diagram is shown in Fig. 27.6. It is quite complicated at first sight, but actually is a combination of five simple peritectic diagrams.

The following phases can form in copper-zinc alloys in the solid state:

(1) α-solid solution of zinc in copper; the solubility of zinc in copper at room temperature is 39 per cent, it remains at that level on heating to 454°C, and drops down to 32 per cent at 902°C;

(2) β-solid solution based on CuZn compound with type (3/2) (number of electrons to number of atoms) electronic bond; it has a simple b.c.c. lattice; the ordered arrangement of atoms remains only at temperatures not above 454-468°C, at higher temperatures the copper and zinc atoms in the b.c.c. lattice have a statistic arrangement; an ordered β-solid solution is designated as β′;

(3) γ-solid solution based on Cu_5Zn_8 compound with type (21/13) electronic bond and a complex cubic lattice; the ordering temperature of this phase is 270°C;

(4) ε-solid solution based on $CuZn_3$ electronic compound (7/4) with a h.c.p. lattice;

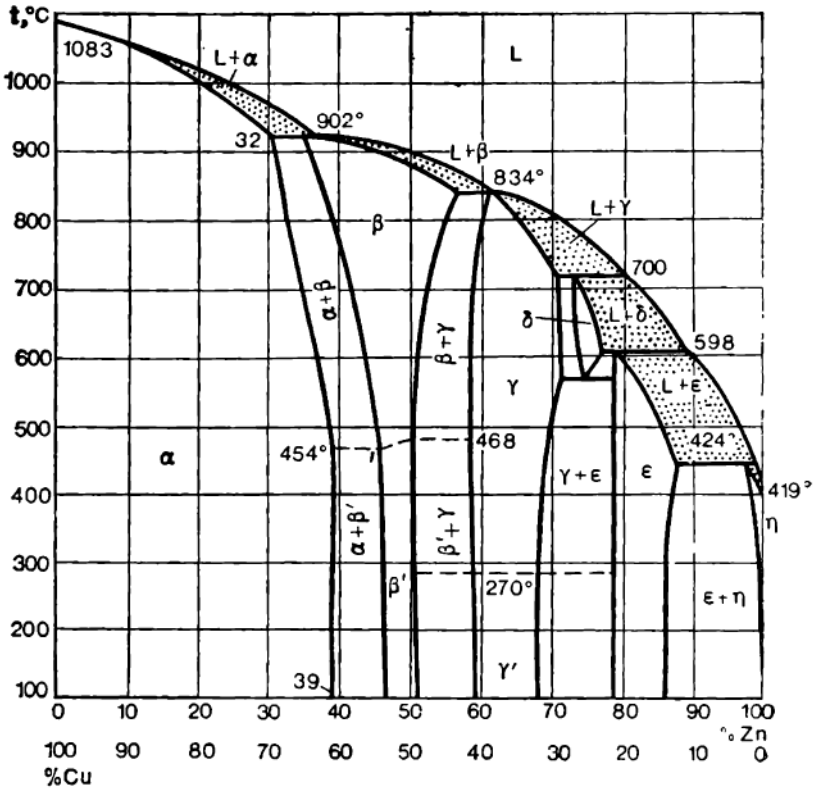


Fig. 27.6. Cu-Zn constitutional diagram

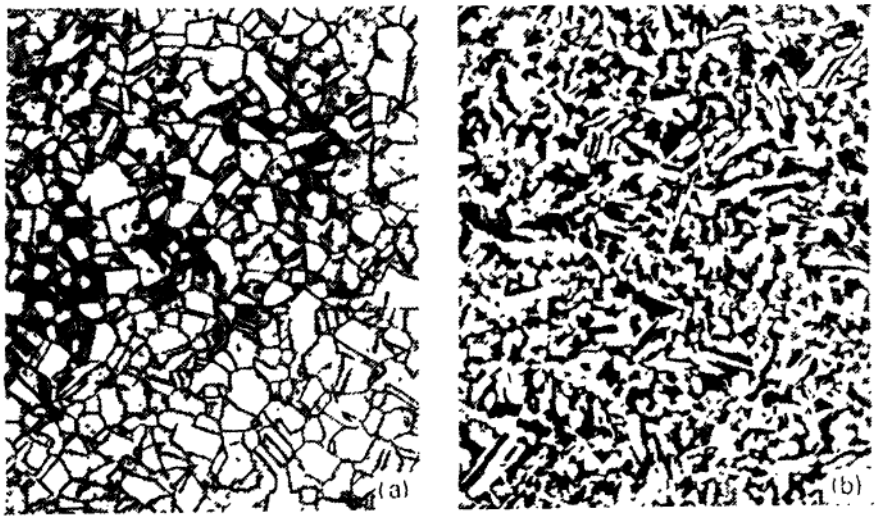


Fig. 27.7. Microstructures of brasses. ×200
(*a*) α-brass; (*b*) α + β-brass

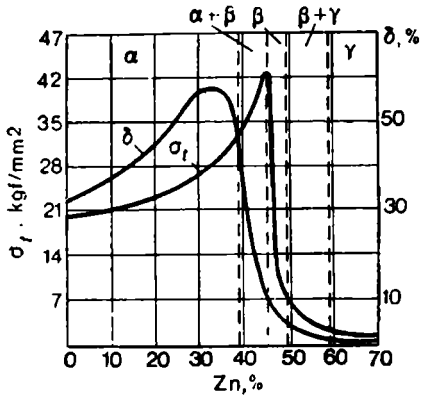


Fig. 27.8. Mechanical properties of Cu-Zn alloys

(5) δ-solid solution based on a compound whose nature is not yet established definitely; and

(6) η-solid solution of copper in zinc.

Thus, β-, γ-, and ε-phases in copper-zinc alloys correspond in their nature respectively to β-, γ-, and ε-phases of compounds with an electronic type of bond (see Sec. 4.6).

At room temperature all brasses consist either solely of α-crystals (Fig. 27.7*a*) or are mixtures of α- and β-crystals (Fig. 27.7*b*).

The mechanical characteristics of Cu-Zn alloys depending on zinc content are shown in Fig. 27.8. Addition of zinc increases the strength and plasticity of alloys. A Cu — 30% Zn alloy has the highest strength among brasses.

The plasticity drops down abruptly on passage through the single-phase boundary (39% Zn); β-brass has the highest strength (σ_t = = 42 kgf/mm²) at a relatively low plasticity (δ ~ 7%); γ-brass is rather brittle. In view of these circumstances (low plasticity), β-brasses, as well as γ- and γ + β-brasses, have no practical application and only brasses having the structure of α or α — β are employed.

The casting properties of brasses are determined by the mutual position of the liquidus and solidus lines. Since the liquidus and solidus lines of the α- and β-phase are very close to each other, the casting properties of brasses can be characterized by a low susceptibility to segregation, high fluidity, and the capacity to form a concentrated shrinkage cavity on solidification.

Brass can be easily plastic worked and is rolled into sheets, strips, shaped sections, etc.

Various brasses show a specific behaviour in hot working. α-brasses, which are plastic at room temperature, turn out to be less plastic than β-brasses in the temperature interval from 500 to 700 C. Though the strength of α-brass at room temperature is lower than that of β-brass the latter turns out to be less strong and more plastic at temperatures above 500°C. In that connection the brasses that are most suitable for hot plastic working are high in zinc (more than 32-39% Zn), so that their structure at the temperature of hot working consists of α + β- or β-crystals (see Fig. 27.6). On the contrary, for the manufacture of thin sheets and wire (i.e. for deformation in the cold state) it is favourable to use brasses having the highest plasticity at room temperature (i.e. single-phase α-brasses with a content of zinc near 30%).

Bismuth and lead impurities in brass can have an adverse effect on the deformability in hot state. The cause for this should be sought in the formation of low-melting inclusions of these metals on the grain boundaries. Lead, however, affects only α-brass which undergoes no phase transformations (Zn < 32%). With a higher content in zinc, the lead that has precipitated on the grain boundaries passes into the body of grains owing to the α → β recrystallization and

thus becomes harmless for plastic working. For that reason, brasses with 32-38% Zn allow an appreciably greater contamination with lead and those with more than 38-40% Zn are intentionally alloyed with up to 1-2% Pb, since they are plastic worked in the single-phase β-state in which lead cannot be an obstacle for plastic deformation. On the other hand, separate lead inclusions facilitate chip breaking and thus improve the machinability of brass.

Brasses are designated by a letter 'Л' and a number showing the average content of copper in an alloy. Since zinc costs less than copper, high-zinc brasses are less expensive.

Commercial brasses are divided into two groups according to the structure they have at room temperature: α-brasses and α + β-brasses. The former contain not less than 61 per cent copper. They are manufactured in the form of thin sheets, strips and other types of semi-product for further stamping or die-forging. High-copper α-brasses (Л80) resemble gold in their colour and are used in jewelry and decorations. High-copper brass is called *tombac*.

Brasses of the second group (α + β-brasses) contain 55-61% Cu; the most popular Grade is Л59; α + β-brasses are rolled into rods from which various parts are then made by machining.

The mechanical strength of brasses is not high. The following characteristics are typical of α-brasses: $\sigma_t = 30$ kgf/mm² and $\delta =$ = 40 per cent; α + β-brasses have a slightly higher strength ($\sigma_t = 35$ kgf/mm²), but a lower plasticity ($\delta = 20\%$).

In addition to simple brasses which are alloys of only copper and zinc, use is also made of special brasses in which various elements are introduced to form some particular properties: lead for better machinability (Grade ЛС59 brass contains roughly 40% Zn and 1-2% Pb and is called *free-cutting brass*); tin to increase the corrosion resistance in sea water (*naval brass*); aluminium and nickel to improve mechanical properties, etc.

Table 27.4. Compositions and Properties of Binary α-Brasses (GOST 17711—72)

Brass Grade	Composition [1], %		Mechanical properties		Brass Grade	Composition [1], %		Mechanical properties	
	Cu	impurities	σ_t, kgf/mm²	δ, %		Cu	impurities	σ_t, kgf/mm²	δ, %
Л96	95-97	0.2	24	52	Л70	69-72	0.2	32	55
Л90	88-91	0.2	26	44	Л68	67-70	0.3	33	56
Л85	84-86	0.3	28	43	Л62	60.5-63.5	0.5	36	49
Л80	79-81	0.3	31	52					

[1] Balance zinc.

Tables 27.4 and 27.5 give respectively the compositions and mechanical properties of simple brasses (binary α-brasses) and of selected complex special brasses.

Table 27.5 indicates also the structural classes to which particular grades of brass belong (for complex brasses this cannot be determined from the Cu-Zn constitutional diagram, since other alloying elements change the boundaries between phase regions).

In particular, an addition of any element (except for nickel) is equivalent to increasing the zinc content. In other words, in the presence of a third element, β-phase appears at a lower content of zinc. L. Guillet has established certain coefficients (10 for Si, 5 for Al, 2 for Sn and Mg, 1 for Cd, Pb, and Fe, 0.5 for Mn, and —1.5 for Ni) in order to evaluate the effect of these elements. For instance, if a brass contains 38% Zn and 2% Sn, it can be approximately regarded as a brass with 42% Zn (it is actually an α + β-brass, but not α-brass).

Table 27.5. Compositions and Properties of Complex Brasses (GOST 17711—72)

Brass Grade	Structure	Composition [1], %		Mechanical properties	
		Cu	alloying elements	σ_t, kgf/mm²	δ, %
ЛС74-3	α	72-75	2.4-3.0 Pb	35	50
ЛС64-2	α	63-66	1.5-2.0 Pb	33	55
ЛС63-3	α+β	62-65	2.4.3.0 Pb	35	50
ЛС60-1	α+β	59-61	0.6-1.0 Pb	35	50
ЛС59-1	α+β	57-60	0.8-1.9 Pb	40	45
ЛО90-1	α	88-91	0.25-0.75 Sn	28	50
ЛО70-1	α	69-71	1.0-1.5 Sn	35	60
ЛО62-1	α+β	61-63	0.7-1.1 Sn	40	40
ЛО60-1	α+β	59-61	1.0-1.5 Sn	38	40
ЛА77-2	α	76-79	1.75-2.5 Al	40	55
АН65-5	α	64-67	5.0-6.5 Ni	40	65
ЛМц58-2	α+β	57-60	1.0-2.0 Mn	44	40
ЛК80-3	α+β	79-81	2.5-4.0 Si	30	58
ЛАЖ60-1-1	α+β	58-61	0.75-1.5 Fe 0.75-1.5 Al	45	45
ЛАН59-3-2	α+β	57-60	2.0-3.0 Ni 2.5-3.5 Al	45	45
ЛЖМц59-1-1	α+β	57-60	0.6-1.2 Fe 0.5-0.8 Mn	45	50
ЛМп-А57-3-1	α+β	55-58.5	2.5-3.5 Mn 0.5-1.5 Al	55	30

[1] Balance zinc.

27.3. COPPER-TIN ALLOYS (TIN BRONZES)

An analysis of copper-tin alloys (*tin bronzes*) should be made by referring first to the Cu-Sn constitutional diagram[1] (Fig. 27.9). Like Cu-Zn diagram, it is a combination of several peritectic diagrams.

The following phases can exist in the solid state in the Cu-Sn system:
(1) α-solid solution of tin in copper;
(2) Sn—this is almost pure tin, since the solubility of copper in tin is probably less than 0.01 per cent and is not indicated in the diagram;
(3) β-solid solution based on β-electronic Cu_5Sn compound; the dotted line indicates the ordering process;
(4) δ-electronic $Cu_{31}Sn_8$ compound;

[1] The Cu-Sn constitutional diagram has been studied by many researchers, but the problems of the actual position of equilibrium lines and of the nature of the phases formed are not yet solved definitely because the diagram is very complex (especially in the concentration region from 20 to 50% Sn) and it is difficult to establish the equilibrium state (in view of the slow diffusion of tin in copper). It may be noted, for instance, that S. T. Konobeevsky has found the value of solubility of tin in copper that is appreciably lower than that given in Fig. 27.9. This result has been obtained by using diffusion annealing of an exceptionally long duration. The real structures of bronzes can be more conveniently analysed by reference to the diagram in Fig. 27.9.

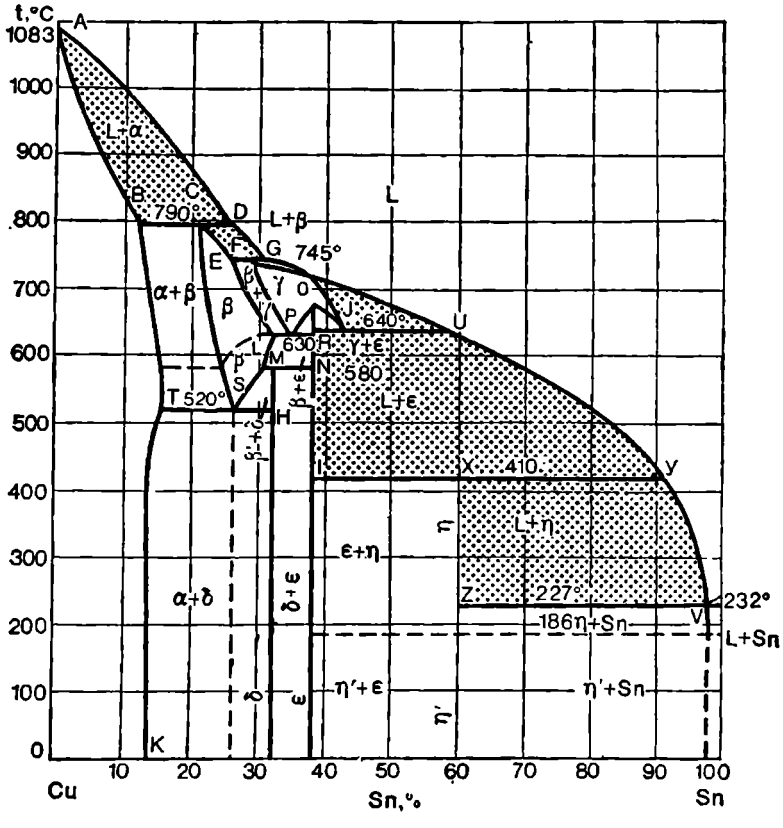


Fig. 27.9. Cu-Sn constitutional diagram

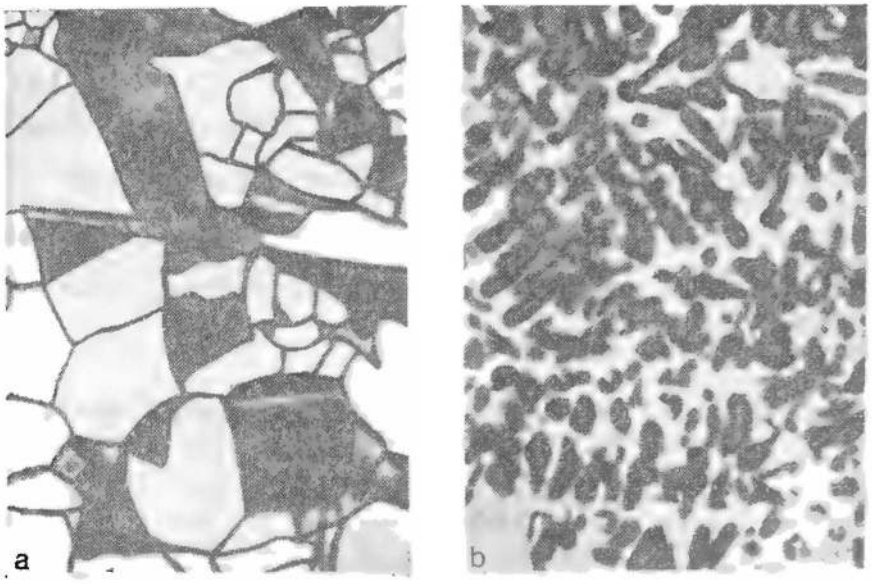


Fig. 27.10. Structures of cast bronze with 6% Sn. ×200
(*a*) as annealed; (*b*) prior to annealing

(5) γ-solid solution based on a compound of copper and tin, with the crystal lattice similar to that of δ;
(6) ε-electronic Cu_3Sn compound; and
(7) η-chemical Cu_6Sn_5 compound.

The structure of cast copper-tin alloys deviates substantially from the equilibrium state[1], so that alloys with 5 or more per cent Sn in as-cast state exhibit the presence of the δ-phase in the form of a eutectoid component (the eutectoid forms at 520°C and has a concentration of 26.8% Sn).

Annealed bronze with up to 14% Sn should have the structure of a homogeneous α-solid solution (Fig. 27.10*a*). In as-cast state, however, the structure of a bronze with up to 5-6% Sn consists of an inhomogeneous α-solid solution which has a dendritic structure as in cast metal (Fig. 27.10*b*).

With a tin content above 6 per cent, tin-high portions of the inhomogeneous α-solid solution (bright portions in Fig. 27.11) may be interlaced with portions of α + δ-eutectoid.

The presence of the brittle δ-phase makes rolling impossible. This is why bronzes with more than 5-6% Sn are neither rolled nor forged but are used only for casting.

The high casting properties of bronzes are mainly due to their exceptionally low shrinkage. The shrinkage of tin bronzes is less

[1] On the causes of this deviation in casting alloys see Sec. 5.10.

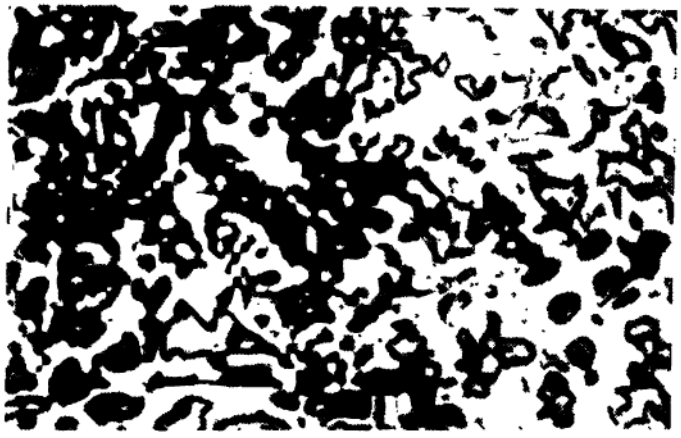


Fig. 27.11. Structure of cast bronze with 10% Sn. ×200

than 1 per cent, compared to roughly 1.5 per cent of cast iron and more than 2 per cent of steels. The most intricate castings (including art castings) are usually made of bronze.

The fluidity of bronze is not high, owing to the large temperature interval between the liquidus and solidus lines. For the same reason, bronze forms no concentrated shrinkage cavity on solidification.

The effect of tin on the mechanical properties of copper is similar to that of zinc, but is more pronounced (Fig. 27.12). A drop in plasticity is noticeable already at 5% Sn. The strength begins to fall off at 20% Sn, when the structure contains too much of the brittle δ-phase.

Inclusions of the hard eutectoid in as-cast bronze ensure a high resistance to abrasion wear, because of which a bronze with 10% Sn is the best antifriction material and is widely employed as a ball-bearing alloy.

Bronzes possess a high chemical stability and are widely used for making fittings (for steam and water pipelines and the like). Thus, the main applications of bronzes are in intricate castings, ball-bearing races, and fittings.

Most commercial bronzes are made less expensive by the additions of 5-10% Zn. In concentrations up to that level, zinc can be dissolved completely in copper and thus has no substantial effect on the structure.

To improve the machinability, bronzes are alloyed with 3-5% Pb; lead is present in the structure in the form of separate lead inclusions which facilitate chip breaking.

Phosphorus is added to bronzes as a deo-

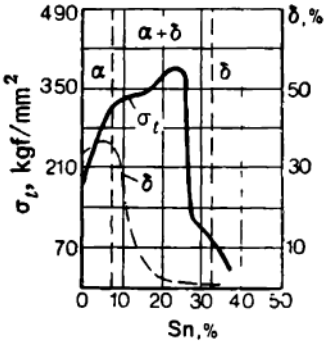


Fig. 27.12. Mechanical properties of Cu-Sn alloys

xidant and to eliminate brittle inclusions of tin oxide (SnO). Bronzes with a phosphorus content near 1 per cent are often called *phosphor bronzes.*

Bronzes are marked with letters 'Бр'; other letters and numerals in a grading give the percentage of particular alloying elements.

Table 27.6 gives the compositions of the most popular commercial tin bronzes and their average mechanical properties in sand-cast specimens.

Table 27.6. Compositions and Properties of Tin Bronzes

Bronze Grade	Composition, %					Mechanical properties		Principal applications
	Sn	Zn	Pb	Ni	P	σ_t, kgf/mm²	δ, %	
Бр010	9-11	—	—	—	—	25	5	Shaped castings, bearings, gear wheels
Бр010-1	9-11	—	—	—	0.8-1.2	25	5	Ditto
БрОЦСН3-7-5-1	2.5-4	6-9.5	3-6	0.5-2	—	20	10	Water and steam fittings, gear wheels
БрОЦС5-5-5	4-6	4-6	4-6	—	—	17	8	Ditto
Бр-1	4-7	5-8	1.4	—	—	—	—	Art castings
БрОФ4-0,25	3.5-4	—	—	—	0.1-0.25	35	50	Sheets, strips, wire (can be plastic worked)
БрОЦ4-3	3.5-4	2.7-3.3	—	—	—	32	40	Ditto

27.4. ALLOYS OF COPPER WITH ALUMINIUM, SILICON, BERYLLIUM AND OTHER ELEMENTS

Alloys of copper with aluminium, silicon, beryllium and other elements are also called bronzes, more particular, aluminium bronze, silicon bronze, etc. to distinguish them from tin bronzes. All these alloys are inferior to tin bronze as regards the casting shrinkage, but excel tin bronze in some particular respects: in mechanical properties (aluminium and silicon bronzes), chemical stability (aluminium bronze), fluidity (Si-Zn bronze). Since tin is expensive, all these bronzes (naturally except for beryllium bronze) are cheape than tin bronze.

Beryllium bronze can be distinguished by high values of hardness and elasticity from other bronzes.

Aluminium bronzes with 5-10% Al possess valuable mechanical and process properties. They crystallize in a narrow temperature interval (Fig. 27.13) and therefore, have a high fluidity and form a concentrated shrinkage cavity.

In addition to simple aluminium bronzes, complex aluminium bronzes have come into use. The compositions and properties of selected aluminium bronzes are given in Table 27.7.

Table 27.7. Compositions and Properties of Aluminium Bronzes (GOST 18175—72)

Bronze Grade	Composition, %				Mechanical properties (as annealed)	
	Al	Mn	Fe	Ni	σ_t, kgf/mm²	δ, %
БрА7	6-8	—	—	—	42	70
БрАМц9-2	8-10	1.5-2.5	—	—	50	55
БрАЖН10-4-4	9.5-11	—	3.5-5.5	3.5-5.5	65	40

Bronzes with 10 or more per cent Al contain in their structure the $\alpha + \gamma$-eutectoid which forms through decomposition of the β-phase.

With fast cooling, the β-phase is undercooled and decomposes with the formation of more disperse $\alpha + \gamma$ particles (i.e. the eutectoid mixture becomes more disperse and more hard as the rate of cooling increases). The rate of decomposition of β-solid solution depends on temperature and can be represented by a C-shaped curve (Fig. 27.14). The heat treatment of aluminium bronzes is similar to that of steels also in that at the critical rate of cooling the β-phase forms an acicular structure. The transformation proceeds following the martensitic mechanism.

Typical microstructures of aluminium bronzes are shown in Fig. 27.15. The structure in Fig. 27.15*a* has been formed by slow cooling from a temperature above the critical one. It is a hypoeutectoid structure consisting of α-crystals (bright) and $\alpha + \gamma$-crystals (dark). The martensitic structure in Fig. 27.15*b* has been formed by water quenching from 900°C.

Aluminium bronzes are used for making various sleeves, guides, seats, flanges, gear wheels and many other critical small parts.

Silicon bronzes, such as Grade БрКЦ4-4 (4% Si, 4% Zn) are used as substitutes for tin bronzes (for instance, Grade БрОЦС5-5-5). Silicon bronzes have a higher shrinkage on casting than tin bronzes, but excel the latter in corrosion resistance, mechanical characteristics, and the density of castings.

Beryllium bronze (БрБ2, 2% Be) is of a special interest. As may be seen from the diagram in Fig. 27.16, an alloy of copper and 2% Be is a precipitation-hardening alloy. The solubility of beryllium in copper at room temperature does not exceed 0.2 per cent, but hardening from 800°C can fix the supersaturated α-solution. If the hardened alloy is then aged artificially at 300-350°C, its hardness will rise to 350-400 *HB*.

Owing to its high strength, elasticity and chemical stability and good weldability and machinability, beryllium bronze is a suitable material for making springs, diaphragms, spring contacts and other parts for critical applications[1].

[1] Further, beryllium bronze can be used for making non-sparkling tools for application in explosion-hazardous mining operations.

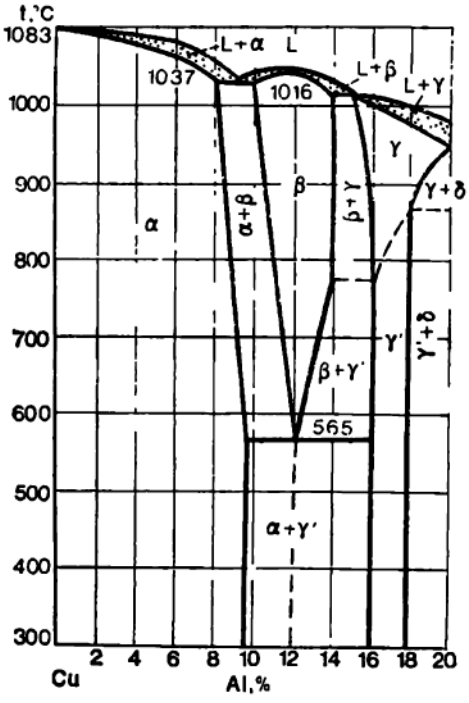


Fig. 27.13. Cu-Al constitutional diagram

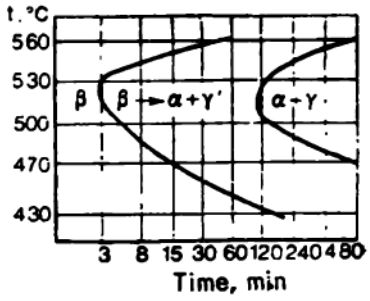
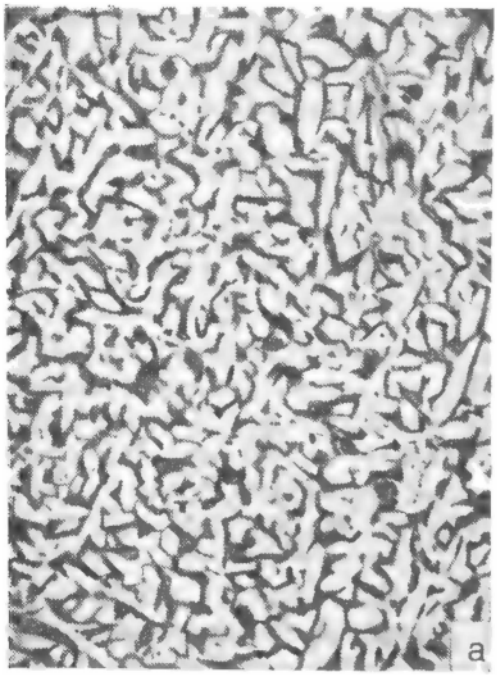


Fig. 27.14. Diagram of isothermal decomposition of β-phase in aluminium bronze



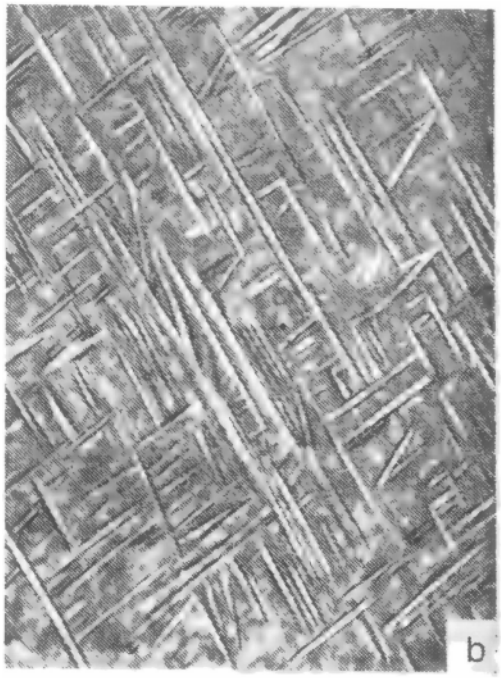


Fig. 27.15. Microstructures of aluminium bronze with 10.5% Al. ×100
(*a*) upon slow cooling from 900°C (α + eutectoid); (*b*) upon fast cooling (martensite)

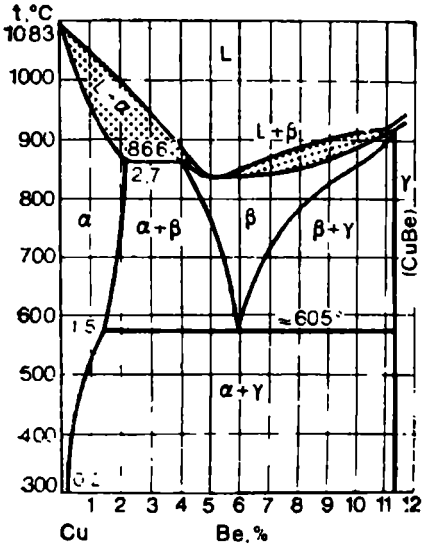


Fig. 27.16. Cu-Be constitutional diagram

Fig. 27.17. Microstructure of lead bronze БрС30. ×100

The composition, heat-treatment conditions and mechanical properties of beryllium bronze are given in Table 27.8.

Table 27.8. Heat Treatment and Mechanical Properties of Beryllium Bronze (1.9-2.2% Be)

Heat treatment	Mechanical properties		
	σ_t, kgf/mm²	δ, %	*HB*
Water quenching from 800°C	50	30	100
Ditto+ageing at 325°C	120	4	370

Lead bronze with 30% Pb (Grade Бр.С30) is a high-quality antifriction material used widely in mechanical engineering.

The structure of this alloy consists of separate grains of copper and lead (Fig. 27.17). Uniformly distributed lead inclusions ensure high antifriction properties of the alloy.

It is however difficult to obtain an appropriate structure in lead bronze, since the wide temperature interval of crystallization (954-326°C, see the Cu-Pb constitutional diagram in Fig. 27.3*b*) and a large difference in the density of copper and lead favour an intensive density segregation. This phenomenon can be avoided by quick cooling of the alloy during crystallization.

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Chapter 28

BEARING ALLOYS AND SOLDERS

28.1. THE PROPERTIES REQUIRED OF BEARING ALLOYS

Despite the increasing application of antifriction (ball and roller) bearings in various machines, sliding bearings are still used quite widely.

Special alloys for making bushings of sliding bearings are called *bearing alloys*. The materials used for the purpose include cast irons, bronzes and low-melting alloys based on lead, tin, zinc or aluminium (called *babbits*).

The metal of a bushing should possess the following properties:

(1) a low coefficient of friction on steel surfaces;

(2) wear of both contacting surfaces should be as low as possible; and

(3) the material should be capable of withstanding substantial pressures.

The first and the second requirement can be well satisfied if the surfaces of a shaft and bushing are separated by a film of lubricant. If the structure of the bushing metal consists of a soft base and hard inclusions, the latter will come to the surface after a short time of operation and form a microrelief which can retain the lubricant (this is called the *Charpy principle*).

Such a structure is formed in certain tin- and lead-base alloys, which however have a low strength and therefore cannot withstand high pressures; further, their low melting point precludes their operation at elevated temperatures.

Cast-iron bushings are made of pearlitic grey cast iron (Grades АЧЦ-1 and АЧЦ-2) which is the cheapest material for making bushings. It can withstand substantial pressures, but has a higher coefficient of friction than bronzes or babbits and for that reason cannot be recommended for use in high-speed engines.

Bronze bushings are made of tin or lead bronzes which have been discussed in the previous chapter. Bronze bushings can well retain the lubricant owing to the inhomogeneous structure of the metal (the structure of tin bronze consists of a soft base of α-solid solution and hard inclusions of $\alpha + \delta$ eutectoid). Bronzes have a high strength. In view of the foregoing they can be used in critical heavy-duty bearings (for high pressures and high r.p.m.).

With the use of very soft low-melting bearing alloys, shaft necks suffer less from wear. In addition, babbits have a lower coefficient of friction compared to steels and can well retain the lubricant. For these reasons low-melting alloys on the basis of tin and lead, and also of zinc and aluminium are used widely as bearing alloys along with cast irons and bronzes.

28.2. LOW-MELTING BEARING ALLOYS (BABBITS)

The group of low-melting bearing alloys includes alloys of the systems Pb-Sb, Sn-Sb and Pb-Sn-Sb, and also zinc-base babbits (with additions of copper and aluminium) and aluminium-base babbits (with additions of copper, nickel, and antimony).

The Pb-Sb constitutional diagram is shown in the actual form (with due regard of Sb in Pb and Pb in Sb solubilities) in Fig. 28.1.

The hardness of lead is around 3 *HB* and that of antimony, 30 *HB*. The eutectic in the system consists of 13% Sb and 87% Pb and has a hardness of 7-8 *HB*. Evidently, hypoeutectic alloys, i.e. those having the structure of eutectic — lead, are too soft for the purpose, whereas hypereutectic alloys with 16-18% Sb are the best in the system. The eutectic forms a soft base and Sb crystals whose concentration is near 5 per cent of the alloy volume serve as hard inclusions.

In the Sn-Sb system (Fig. 28.2), tin has a low hardness, some 5 *HB*. An optimal composition of alloy contains 13% Sb and 87% Sn and has a two-phase $\alpha + \beta'$ structure. i.e. tin-base α-solid solution (soft base) and β'-solid solution based on SnSb intermetallic compound (hard inclusions).

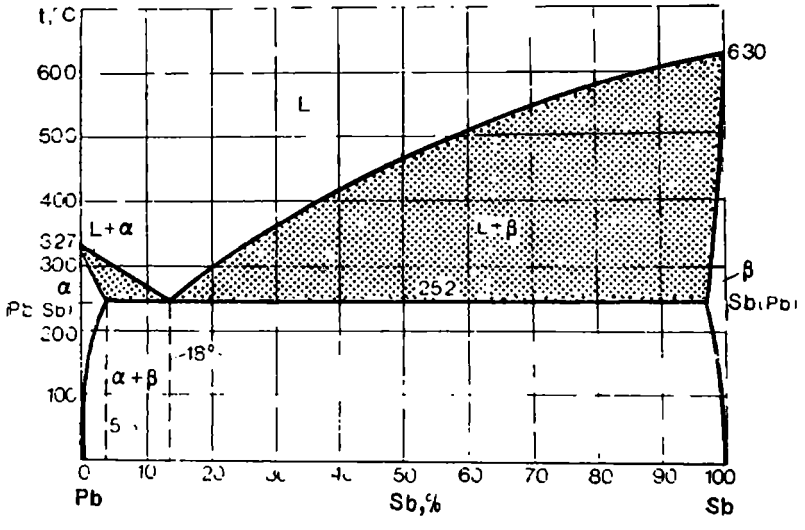

Fig. 28.1. Pb-Sb constitutional diagram

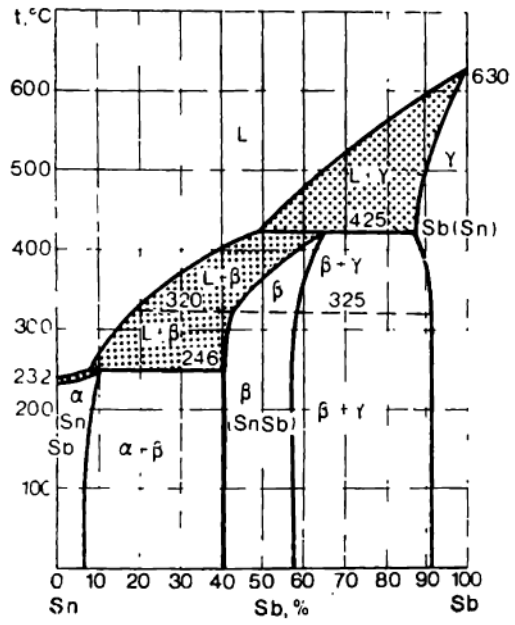

Fig. 28.2. Sn-Sb constitutional diagram

Fig. 28.3. Microstructure of Б83 babbit. ×100

In an Sn-Pb-Sb bearing alloy, the soft base is the lead-base solid solution and particles of SnSb compound are hard inclusions. All the alloys mentioned usually have an addition of copper which on the one hand inhibits density segregation and, on the other, forms hard inclusions of Cu_3Sn compound.

A typical structure of Sn-Sb-Cu babbit Grade Б83 (its composition see in Table 28.1) is shown in Fig. 28.3 where cubic inclusions of SnSb compound and finer Cu_3Sn inclusions are seen on the dark background of α-solid solution. Overheating forms coarser inclusions and impairs the quality of the alloy.

The compositions of babbits given in Table 28.1 can be divided into three groups: Sn-Sb alloys (Grades Б83 and Б89), Pb-Sn-Sb (БС, БТ, БН, and Б16) and lead babbits which contain no tin. In the second group, Grades БС, БН and БТ contain additions of other elements besides tin, antimony and copper. These additions are made for different purposes; for instance, arsenic improves fluidity (which facilitates casting of bushings), nickel increases hardness and therefore reduces wear; cadmium has the same effect as nickel. The role of tellurium and arsenic is to form fine hard inclusions (TePb and AsPb) which increase wear resistance of the alloy.

The best qualities are shown by Sn-Sb babbits (Б83 and Б89). The tin base in them is tough and plastic and only slightly susceptible to fatigue failure. Then comes Grade Б16, an Sn-Pb-Sb babbit with lead as the soft base. Sn-Pb-Sb babbits are substantially less expensive than Sn-Sb grades and are slightly inferior to the latter in quality. A poorer alloy is Pb-Sb babbit (БС) in which the eutectic base is insufficiently plastic.

Grade БК babbit, which is used in railway transport, and also Grade БС babbit, is a relatively cheap alloy: its structure consists of lead (the base) and hard inclusions of compounds of lead with calcium and sodium.

Table 28.1. Compositions and

Babbit Grade	Composition, %					
	Sn	Sb	Cu	Pb	other elements	total impurities (maximum)
Б83	Base	10-12	5.5-6.5	—	—	0.55
Б89	Ditto	7.25-8.25	2.5-3.5	—	—	0.55
Б6	5-6	14-16	2.5-3.0	Base	1.75-2.25 Cd	0.4
БТ	9-11	14-16	0.7-1.1		0.05-0.20 Te	0.6
БН	9-11	13-15	1.5-2.0	Ditto	0.5-0.9 As 0.75-1.25 Ni 1.25-1.75 Cd	0.35
Б16	15-17	15-17	1.5-2.0	Ditto	—	0.6
БС	—	16-18	1.0-1.5	Base	—	0.5
БК	—	—	—	Ditto	0.85-1.15 Ca 0.6-0.9 Na	0.7

Note: The solubility in tin, lead and chemical compounds is not indicated;

The deficiency of tin (and also of lead) necessitates the search for alloys based on other, less scarce metals (zinc, aluminium).

Examples of zinc-base bearing alloys are Grades ЦАМ10-5 and ЦАМ5-10; their compositions, structure and properties are given in Table 28.2.

Zinc-base babbits ЦАМ10-5 and ЦАМ5-10 are inferior to tin-base babbits in plasticity, friction coefficient and linear expansion and are almost equivalent to lead-base babbits.

Table 28.2. Compositions and Properties of Zinc Babbits

Babbit Grade	Composition, %		Properties				
	Al	Cu	γ, g/cm^3	$t_{m.p.}$, °C	δ, %	coefficient of friction	$\alpha \times 10^6$
ЦАМ10-5	10	5	6.3	395	0.5	0.009	27
ЦАМ5-10	5	10	7.1	500	1	—	28

Notes: 1. The structure of these alloys consists of soft $Zn + Al - CuZn_3$ eutectic and hard $CuZn_3$ inclusions.

2. The ultimate strength of these alloys is 30 kgf/mm^2.

Structures of Babbits

Structure		Properties					
soft base	hard inclusions	γ, g/cm³	$t_{m.p.}$, °C	σ_t, kgf/mm²	δ, %	coefficient of friction (with lubricant)	$\alpha \times 10^6$
Sn	SnSb, Cu_3Sn	7.4	380	9	6	0.005	21
Sn	Cu_3Sn	7.3	342	9	9	—	—
Pb	SnSb, Cu_3Sn	9.6	460	7	0.5	0.005	21
Pb	SnSb	—	—	8	2	0.009	23
Pb	SnSb, $SnAs_2$	9.5	400	7	1	0.006	—
Pb	SnSb, Cu_3Sn	9.3	410	8	0.5	0.006	24
Pb+Sb-eutectic	Sb	10.1	410	4	0.5	0.007	26
Pb	Pb_3Ca, Pb_3Na	10.5	470	10	2.5	0.004	26

actually these phases are compound-base solid solutions.

There is a series of aluminium alloys which are used as bearing alloys. These are two-phase high-alloyed alloys in which the aluminium-base solid solution is the soft base with hard inclusions of chemical compounds. The compositions and selected properties of aluminium bearing alloys are given in Table 28.3.

Aluminium bearing alloys possess high operating properties (a low coefficient of friction and high wear resistance), but are inferior to common babbits in technological properties. Their high hardness is a drawback, rather than an advantage, since necessitates a higher surface finish in the machining of shafts and bushings and a higher hardness of the shaft neck metal; otherwise, quick wear is probable. The high coefficient of linear expansion of aluminium babbits requires a more careful assembly with large tolerances.

Aluminium babbits are used as substitutes for tin- and lead-base babbits and tin bronzes.

In addition to the aluminium alloys given in Table 28.3, aluminium-tin bearing alloys are coming into use as bearing alloys; they contain 6-7% Sn and additions of other elements, such as nickel, copper, or silicon, in amounts of 1 to 2 per cent.

28.3. SOLDERS

There are two types of solder:

Soft solders which have a low melting point and can ensure only the tightness of soldered seams. Soldered seams usually have very

Table 28.3. Compositions and Properties of Aluminium Babbits

Babbit Grade	Composition, %						Hard inclusions	Properties				
	Sb	Pb	Mg	Ni	Cu	Si		γ, g/cm^3	$t_{m.p.}$, °C	σ_t, kgf/mm^2	δ, %	$\alpha\times10^6$
ACC6-5	5-6	4-5	0.5-0.7	—	—	—	AlSb	3.1	750	8	14	24
ACM	3.5-5	—	0.5-0.7	—	—	—	AlSb	2.8	750	9	29	24
AH2,5	—	—	—	2.7-3.4	—	—	Al_3Ni	2.85	650	14	23	25.5
Alcusin D	—	—	—	—	7.5-9.5	1.5-2.5	$CuAl_2$	2.85	632	16	1	25.7

Note. The soft base is aluminium.

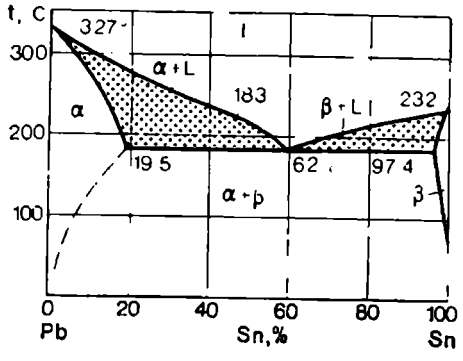

Fig. 28.4. Pb-Sn constitutional diagram

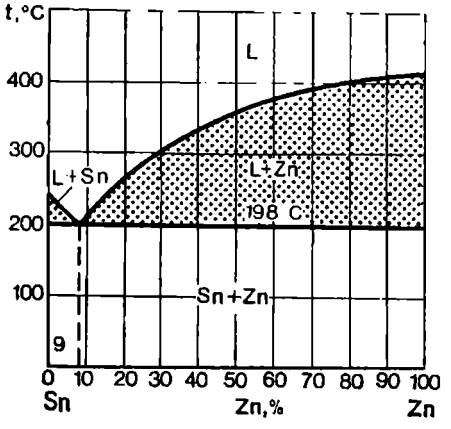

Fig. 28.5. Sn-Zn constitutional diagram

low mechanical characteristics (σ_t = 5-7 kgf/mm^2) and cannot be subjected to mechanical actions.

Hard, or *brazing solders* have a higher melting point than soft ones. They are more difficult to be used in soldering but provide higher mechanical characteristics in soldered seams.

Soft solders are mostly alloys of low-melting metals: lead, tin, bismuth, cadmium; most often alloys of lead and tin. The most low-melting alloy in the Pb-Sn system is the eutectic alloy containing 62% of Sn and 38% Pb (Fig. 28.4), i.e. approximately 2/3 of Sn and 1/3 of Pb; it is often called *quick solder*. Its melting point is 183°C. The standard designation of this alloy is ПОС-61 (where '61' is the average content of tin). Solder Grades ПОС-40 and ПОС-30 contain respectively 40 and 30 per cent tin and have a higher melting point, as may be seen from the diagram in Fig. 28.4.

Hard solders have their melting point usually in the interval of 800 to 900°C and are mostly alloys of copper and zinc (brasses) or of copper, zinc and silver (called silver solders). The latter are used for soldering in electrical instruments, i.e. in the instances where the electric conductivity of soldered seams should be not less than that of the main metal.

Table 28.4. Tin Grades for Soldering and Tinning

Tin Grade	Sn (minimum)	Total impurities (maximum)	Application
01	99.90	0.10	Tinning of steel sheets for food industry
02	99.56	0.44	Tinning of domestic utensils

The compositions of standard alloys for soldering and tinning are given in Tables 28.4 and 28.5. Tin Grades O1 and O2, and also lower-quality Grades O3

Table 28.5. Compositions and Properties of Soft Solders

Solder Grade	Composition[1], %		Properties				
	Sn	Sb	temperature range of solidification, °C	fluidity, cm	ρ, m/ohm mm²	σ_t, kgf/mm²	
						metal	seam
ПОС-90	89-90	<0.15	185-220	135	—	4	—
ПОС-61	56-61	<0.8	183-185	135	6.9	5	4-8
ПОС-50	49-50	<0.8	183-210	115	6.4	4	5-9
ПОС-40	39-40	1.5-2.0	183-235	91	5.7	4	4-11
ПОС-30	29-30	1.5-2.0	183-256	63	5.5	3	3-9
ПОС-18	17-18	2.0-2.5	183-277	60	4.5	3	4-8

[1] Balance lead.

(98.35% Sn) and O4 (96.25% Sn) are used for tinning and for making babbits and solders. The strength of tin at room temperature is near 2.5 kgf mm², whereas the strength of a soldered seam may be 4-9 kgf mm² or even higher, owing to the formation of solid solutions in the base metal.

In addition to the grades given in the tables, other grades of soft solders are used, for instance, low-tin solders ПОС-10, ПОС-5 and some others, which contain only 5-10% Sn and are therefore less expensive, but are inferior in the physical and process properties; low-tin alloys have a higher temperature range of solidification (265-299°C for ПОС-10 and 300-314°C for ПОС-5) and lower values of strength and fluidity.

Tin-zinc solders of the type ПОЦ are also used; they contain 90, 70, 60 or 40% Sn, the balance being zinc (Grades ПОЦ-90, ПОЦ-70, ПОЦ-60, and ПОЦ-40). The best among them is Grade ПОЦ-90 which has a eutectic compo-

Table 28.6. Compositions and Properties of Pb-Ag Solders

Solder Grade	Composition, %			Properties		
	Ag	Sn	impurities (maximum)	solidification range, °C	ρ, m/ohm mm²	σ_t, kgf/mm²
ПСр-1.5	1.3-1.7	0.75-1.25	0.5	309-309	—	—
ПСр-2.5	2.3-2.7	—	0.5	304-304	5.2	3.3
ПСр-3	2.7-3.3	—	0.5	300-305	5.0	3.1

Note. The base is lead.

sition (Fig. 28.5) and the lowest temperature of the beginning of crystallization, which is 198°C in the constitutional diagram but is actually slightly higher (not above 202°C) owing to deviations in the alloys composition. The temperature of the beginning of crystallization for Grades ПОЦ-70, ПОЦ-60 and ПОЦ-40

Table 28.7. Compositions and Properties of Silver Solders (GOST 8190—56)

Solder Grade	Composition, %			Properties	
	Cu	Zn	impurities (maximum)	solidification range, °C	ρ, ohm mm²/m
ПСр-72	27.3-28.5	—	0.25	779-779	0.022
ПСр-50	49.3-50.5	—	0.25	779-850	0.025
ПСр-45	29.5-30.5	24-26.5	0.50	660-725	0.097
ПСр-25	39-41	33.5-37	0.50	745-775	0.069
ПСр-10	52-54	35.5-39	0.50	815-850	0.065

Note. Numbers in designations give the content of silver (the base).

is respectively 325°, 345° and 365°C and the temperature of the end of crystallization is 198°C for all these alloys. Tin-zinc solders have a higher strength and lower plasticity compared to tin-lead alloys.

Lead-silver solders are used for soldering copper and copper alloys in place of tin solders, since tin-containing alloys can form with copper a Cu_3Sn compound which embrittles soldered seams. The compositions and properties of lead-silver solders are given in Table 28.6.

Table 28.7 gives the compositions and properties of selected brazing silver alloys.

Some grades of brasses (which were discussed earlier in this chapter) are also used as brazing alloys in place of expensive silver solders.

28.4. FUSIBLE ALLOYS

This group usually includes alloys whose melting point is below 230°C (i.e. below the melting point of tin). Low-melting metals (lead, tin, bismuth, indium, mercury) are taken as components of these alloys, usually in combinations to form a polyphase multicomponent eutectic (with two, three or more phases).

Table 28.8. Compositions of Fusible Alloys, %

Alloy Grade	Sn	Pb	Cd	Bi	Zn, In	Alloy Grade	Sn	Pb	Cd	Bi	Zn, In
Л199	91.1	—	—	—	8.9 Zn	Л96	18.75	31.25	—	50.0	—
Л183	61.9	38.1	—	—	—	Л68	12.5	25.0	12.5	50.0	—
Л141	50.0	30.0	—	20.0	—	Л58	12.0	18.0	—	60.0	21.0 In
Л145	49.8	32.0	18.2	—	—	Л47	8.3	22.6	5.3	44.7	19.1 In
Л130	52.0	30.0	13.0	5.0	—						

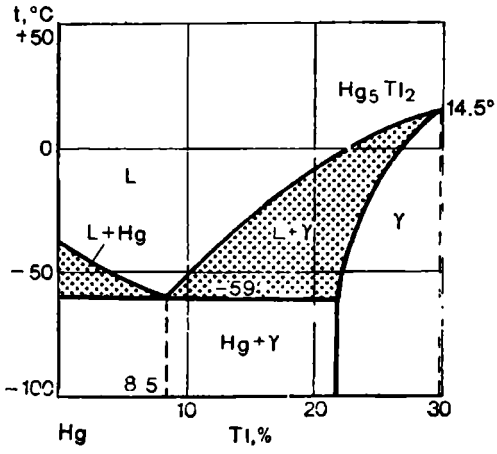

Fig. 28.6. Hg-Tl constitutional diagram

Fusible alloys are employed in electric safety fuses, as especially low-melting solders, as material for anatomic moulds, etc.

Fusible alloys are graded with a letter 'Л' and a number showing the melting point (which is constant, since these alloys are eutectic).

The principal grades of fusible alloys are given in Table 28.8. The tin-lead solders Grades ПОС-90 and ПОС-61 (see Table 28.5) can also be classed with this group. An alloy forming a quarternary eutectic in the Sn-Pb-Cd-Bi system (i.e. the most low-melting alloy in that system) is widely known as *Wood's alloy*; its melting point is 68°C.

Grade Л47 is the eutectic alloy in the quinary Sn-Pb-Cd-Bi-In system; its melting point is 47°C.

Finally, alloys with additions of mercury (*amalgams*) have still lower melting points (alloys of the Sn-Pb-Bi-Hg system). Pure mercury and alloys of the system Tl-Hg melt at temperatures below 0°C. The most low-melting metallic alloy known in nature (an alloy of 8.5% Tl and 91.5% Hg) melts at —59°C (Fig. 28.6).

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Chapter 29

MISCELLANEOUS NON-FERROUS ALLOYS

29.1. ZINC AND ZINC ALLOYS

Zinc has a high density (7.1 g/cm^3), a relatively low melting point (419°C) and a very low boiling point (906°C). It has a low strength (σ_t = 15 kgf/mm^2) and high plasticity (δ = 50%). Zinc has a hexagonal lattice and undergoes no allotropic transformations.

Zinc is employed for hot and electrolytic zincing of steel sheets, in polygraphic industry, for making electrolytic cells, etc. It is also used as an addition to various alloys, in the first place to copper alloys (brasses and the like) and as the base of various zinc alloys[1].

Commercial zinc is graded according to its purity: ЦВ (99.99% Zn), Ц0 (99.96), Ц1 (99.94), Ц2 (99.9), Ц3 (98.7), Ц4 (97.5). The main impurity in commercial zinc is lead; the metal may also be contaminated with iron, cadmium and some other elements.

Aluminium (5-10%) is the most common addition in zinc alloys. The Al-Zn system (Fig. 29.1) can form two solid solutions: β-solid solution (almost pure zinc) and α-solid solution based on aluminium which can dissolve up to 83% Zn (i.e. in the limit it can contain 83% Zn and only 17% Al).

The α-solid solution can decompose in a definite interval of temperatures and concentrations into two solid solutions of the same crystal structure: α_2 which is rich in zinc and α_1 which is low in zinc content.

According to the Al-Zn constitutional diagram (Fig. 29.1), α-solid solution undergoes a monoeutectoid $\alpha_2 \rightarrow \alpha_1 + \beta$ decomposition at 275°C. The solubility of zinc in aluminium decreases sharply on

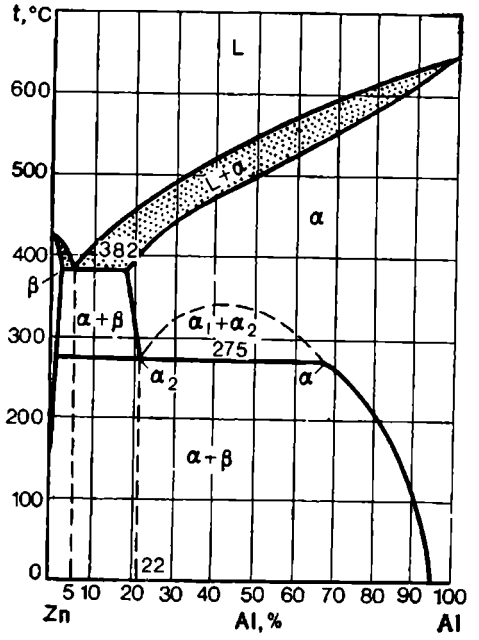

Fig. 29.1. Zn-Al constitutional diagram

[1] Some of them, for instance, zinc-base soft solders and zinc babbits, have been discussed earlier.

lowering the temperature below 275°C. Thus, the structure of alloys of zinc with 5-10% Al consists of hypoeutectoid β-alloy and $(\alpha + \beta)$ eutectoid. Quick cooling can arrest the eutectoid decomposition and undercool the α_2-phase. The structure that is thus formed is unstable and the structural changes that occur (decomposition of the undercooled α_2-phase) cause dimensional changes, which is an unwanted effect, especially in high-precision castings (pressure-die casting). An addition of magnesium (near 0.1%) can lower the rate of decomposition of undercooled α_2-solid solution and produce a stabilizing effect on the dimensions of castings.

Alloys of zinc with copper are not prone to ageing, but have poorer mechanical properties than Zn-Al alloys.

Among zinc-base alloys, the highest strength is shown by ternary alloys of the Zn-Al-Cu system. The structure of these alloys may be diverse (depending on the content of aluminium and copper). It may contain primary β-precipitates (pure zinc), α-phase (high-zinc aluminium base solution), ε-phase ($CuZn_3$ compound), binary eutectics $\beta + \alpha$, $\varepsilon + \alpha$ and $\beta + \varepsilon$ and ternary $\alpha + \beta + \varepsilon$ eutectic. For instance, a casting alloy with 5% Al and 10% Cu has the structure consisting of primary ε-crystals, binary $\varepsilon - \beta$ eutectic and ternary $\varepsilon - \beta - \alpha$ eutectic. The compositions of selected commercial zinc alloys are given in Table 29.1.

Table 29.1. Compositions and Properties of Commercial Zinc Alloys

Alloy Grade	Composition, %			Properties		
	Al	Cu	Mn	σ_t, kgf/mm²	δ, %	*HB*
ЦА4*	3.5-4.5	—	0.03-0.08	25-30	3-6	70-90
ЦАМ4-1*	3.5-4.5	0.75-1.25	0.03-0.08	27-33	2-5	80-100
ЦАМ4-3*	3.5-4.5	2.5-3.5	0.02-0.10	32-38	2-3	80-120
ЦМ1	—	0.8-1.2	—	20-30	30-40	45-75
ЦАМ0,2-4	3.5-4.5	0.20-0.15	—	30-36	20-30	75-90
ЦАМ4-1	3.7-4.3	0.6-1.0	0.02-0.05	37-44	8-12	90-105
ЦАМ10-1	9-11	0.6-1.0	0.02-0.05	40-46	8-12	90-110
ЦАМ15	14-16	—	0.02-0.04	25-40	10-40	40-110

Note. Those marked with an asterisk are used for pressure die-casting, the remaining grades, for rolling or pressing sheets and shaped sections.

29.2. TYPE-METAL ALLOYS

Alloys for type casting should have, if possible, a low melting point and an appropriate hardness; the loss of metal during remelting should be as low as possible. Special alloys based on tin, lead and zinc have been developed for the purpose. Tin-base alloys are not used now, in view of the high cost of tin. Lead-base alloys are employed most often. Zinc-base alloys are less scarce, but have a higher melting point and a higher remelting loss.

Table 29.2. Compositions, %, and Some Properties of Type-metal Alloys

Grade	Sb	As	Sn	Al	Cu	Mg	Pb	Zn	$t_{m.p.}$, °C	*HB* (as cast)
МШ1	13.5-15	3.5-4.5	—	—	—	—	Base	—	325	25-30
МШ2	14-16	2.7-3.3	—	—	—	—	—	—	315	23-28
МШ3	14-16	1.5 2.5	—	—	—	—	Base	—	320	23-30
МЛ1	9.5-10.5	1.0-1.5	—	—	—	—	Base	—	250	—
ЛН1	11-12	—	4.2-4.8	—	—	—	Base	—	245	22-23
ЦШ1	—	—	—	3.5-4.5	< 0.06	0.02-0.06	—	Base	390	—
No.3	—	—	—	2.2-3.0	< 0.10	1.2-1.8	—	Base	400	—
No.7	—	—	—	4.5-5.5	3.5-4.5	1.5-2.0	—	Base	460	—

The compositions of the most common type-metal alloys and some of their properties (melting point and hardness) are given in Table 29.2.

Polygraphic industry also employs an alloy of zinc with small additions of magnesium (0.05%) and aluminium (0.1%); it is called *microzinc*. It has a fine-grained structure and a higher hardness (55-70 *HB*) than the other type-metal alloys.

29.3. NOBLE METALS

This group includes gold, silver, platinum-group metals, and their alloys. Noble metals owe their name to their high corrosion resistance: they do not practically corrode in atmospheric air, water and many other media. All these metals (except for gold and silver) have a high melting point, high density, undergo no allotropic transformations (except for rhodium), and are very plastic (except for rhodium and osmium). All are quite expensive.

Some properties of these metals are given in Table 29.3.

Table 29.3. Properties of Noble Metals

Metal	Lattice type	Density, g/cm³	$t_{m.p.}$, °C	*HB*	Temperature at which oxidation in air begins, °C
Ru	H12	12.5	2 310	200	100
Rh	C12	12.4	1 960	55	600
Pd	C12	12.2	1 550	30	600-800
Ag	C12	10.0	960.5	20	No
Os	H12	22.5	3 050	350	18-20
Ir	C12	22.6	2 443	160	600-700
Pt	C12	21.6	1 769	30	No
Au	C12	19.6	1 063	18	No

Noble metals, in the first place gold and silver, are employed in jewelry and dentistry. Pure gold is not used in view of its softness. Alloying of gold with silver is not very effective, since it raises the hardness only insignificantly (the hardness of Au-Ag alloys does not exceed 30 *HB*). Alloying gold with copper increases its hardness substantially (with 20% Cu, the hardness of alloys is above 100 *HB*). Copper, however, lowers the corrosion resistance of gold. Ternary Au-Ag-Cu alloys are practically used in jewelry and dentistry.

The most popular in jewelry are gold alloys of the purity index of 375, 583, 750 and 916, which means that they contain respectively 375, 583, 750 or 916 g gold per 1 000 g of alloy, the balance being silver and copper in various proportions.

Alloys of purity 916 are the softest and most corrosion-resistant. The corrosion resistance diminishes towards lower purity indices. Alloys of purity index 583 with the Cu:Ag ratio of near 1:1 have the highest hardness (and therefore, the highest wear resistance). These alloys have the natural colour of gold.

The structure of these alloys is either a homogeneous solid solution (high index alloys) or a mechanical mixture of two or three solid solutions.

Annealing of these alloys (for instance, for recrystallization) can cause embrittlement owing to ordering processes (the formation of ordered solid solutions of the type of AuCu or $AuCu_3$).

Whereas gold and silver alloys are mainly employed in jewelry and dentistry, platinum-group metals have found industrial application.

An alloy of 90% Pt and 10% Rh is used for making thermo-couples (one electrode is made of this alloy and the other, of pure platinum); it possesses a high electromotive force and high scale resistance. Pt/Pt-Rh thermo-couples can operate at temperatures up to 1 700°C.

Wires made of noble-metal alloys (for instance, Pt + 25% Ir or Pt + + 30-40% Ag) are used in potentiometer windings of measuring and control precision instruments.

Electric contacts for various critical applications are made of special noble-metal alloys (Pt + Ir, Pt + W, Pd + Ag, etc.) having a high resistance to vaporization and oxidation.

Alloys of Os and In possess the favourable combination of high hardness and wear resistance and very high corrosion resistance. They are used for making pivots of various measuring instruments, compass needles, fountain pen tips, etc.

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Chapter 30

BIMETALS AND COMPOSITE MATERIALS

30.1. TWO- AND MULTI-LAYER METALS [1]

Many properties of metals, in particular, their mechanical properties, are determined by the work of the whole cross-section of a metal part. For instance, if a metal specimen is subjected to tension, all its bulk, both in the core and in surface layers, are stressed to the same value. In other cases, however, the workability of metal parts is determined only by the resistance of the surface layer to external actions. This circumstance is utilized to increase the resistance of a metal to fatigue, wear, corrosion and other types of gradual failure by methods of surface treatment[2] which change the structure and properties of the metal in the surface layers only.

There is another method for improving the surface properties of metals by applying one or more layers of a different metal at an intermediate stage of metallurgical process, i.e. when making sheets, strips, rods, shaped sections, etc. Products made by this method are called *bimetals* and are composed of a layer of base metal and one or two layers of a plated metal applied respectively on one or two sides of the base (Fig. 30.1).

The plated (protective) layer is firmly bonded with the base over the whole surface of contact, i.e. a bimetal is monolithic.

Bimetals are made either by casting or by plastic deformation of packets of sheets; in either case, the plated layer is fused firmly to the base.

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[1] Written together with S. I. Bulat.

[2] Surface hardening (see Ch. 12), chemical heat treatment (Ch. 13) or hard facing (Ch. 20).

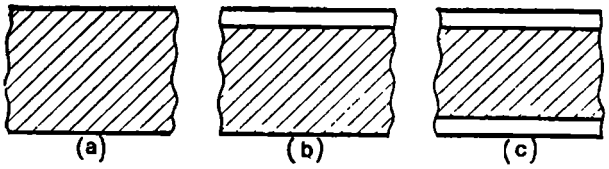

Fig. 30.1. Monometal (*a*), one-side plated bimetal (*b*), two-sides plated bimetal (*c*)

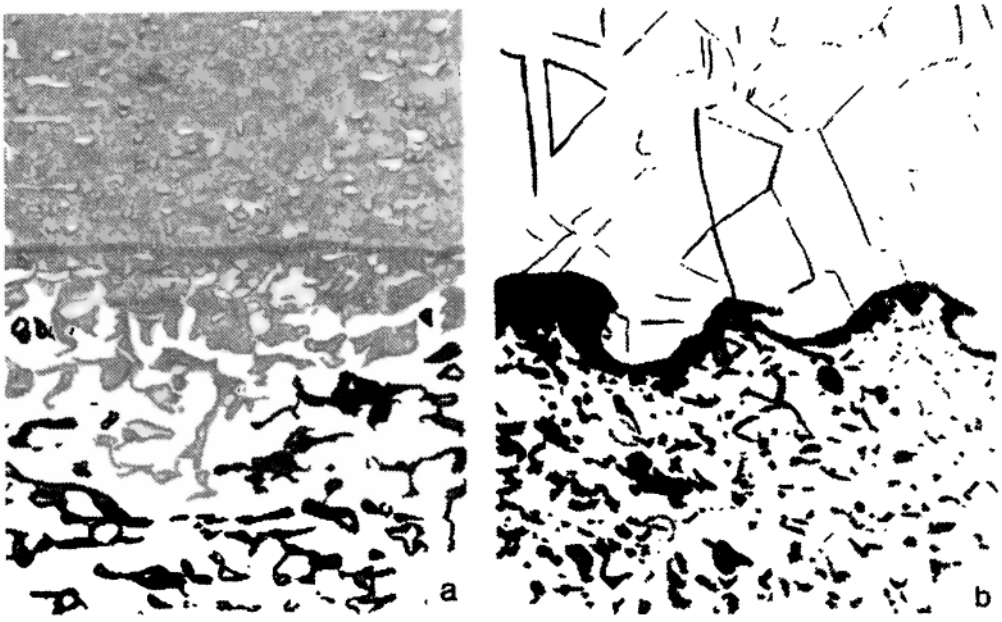

Fig. 30.2. Microstructures of bimetals
(*a*) Ст.3 + Х6Ф1; (*b*) Ст. 3 + Х18Н10Т

An example of bimetal is plated duralumin (see Ch. 26), i.e. the duralumin base is plated with a layer of pure aluminium to improve the corrosion resistance.

Bimetals composed of essentially different metals have found a wide application. For instance, corrosion-resisting bimetals are made by applying a protective layer of stainless steel (Х18Н10Т, Х17Н13М2Т, Х23Н28М3Д3Т, etc.), nickel, monel-metal (Grade НМЖМц-28-2,5-1,5) onto the base of carbon or low-alloy steel; wear-resisting bimetals are made by coating carbon or low-alloy steel with a hard tool steel (such as Grade Х6Ф1). Bimetallic wire is usually steel wire with a copper or aluminium coating.

The main advantage offered by bimetals is a low cost (compared to a product made completely of the expensive metal used in the plated layer)[1].

The ratio of the thicknesses of the layers in a bimetal is of great importance. The thickness of a plated layer is usually 10 to 20 per cent of the total thickness but not less than 1.5-2 mm. It then follows that the manufacture of bimetallic materials can be economically advantageous if the thickness of the sheets produced is not less than 5-10 mm.

In the hot rolling of bimetals, the base and the plating metal are fused together over the whole surface of contact (Fig. 30.2*a*) and thus the roughnesses in their surfaces are filled in (Fig. 30.2*b*), especially if the plating layer has been 'glued' to the base by explosion before hot rolling.

The firmness of adhesion between the base and plating is checked by a shear test; the shear resistance along the base-to-plating interface should be not less than the shear resistance of the weaker metal in the combination.

An important circumstance for the manufacture and (high-temperature) operation of bimetals is the redistribution of the elements between the layers, since the composition of the layers is usually quite different.

As may be seen from Fig. 30.3, the carbon from the plating layer (steel Х18Н10Т) can saturate the base metal (carbon steel Ст3). In some cases the

[1] In less often cases, bimetals can possess certain specific properties which cannot be obtained in a monometal (such as self-sharpening capacity).

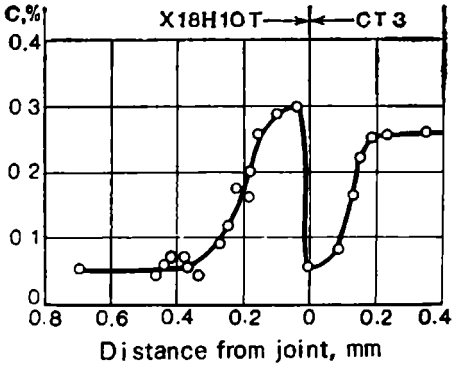

Fig. 30.3. Redistribution of carbon and hardness in the plated layer and base metal upon technological heating

diffusion of elements can result in the formation of brittle phases or in a change of the metal structure at the interface and thus it can impair certain properties, such as corrosion resistance.

These effects can be prevented by using intermediate layers which can prevent diffusion and therefore, redistribution of the elements. For instance, a nickel interlayer can prevent the diffusion of carbon.

As has been shown (S.A. Golovanenko), the diffusion redistribution of elements between the layers in a bimetal can be prevented by an appropriate selection of the materials for the base and plating so as to have the same thermodynamic activity of carbon (or another element) in both.

The use of bimetals in chemical engineering, agricultural machine building and other branches of industry is an effective method for saving expensive materials and increasing the durability of machine elements. The manufacture and application of bimetals have posed a number of specific metallurgical problems which can be characterized in general as the *compatibility* of different materials.

30.2. COMPOSITE MATERIALS[1]

A composite material is a combination of two or more chemically unlike materials with distinct boundaries between them. Composite materials should possess the properties not found in their components taken individually, otherwise the application is senseless.

The designs of new space vehicles, aircraft, rockets, deep-diving apparatus, high-pressure vessels, new types of water and land transport impose certain specific requirements which can be best satisfied by composite materials, and often, only by them.

Composite materials are very diverse but can be divided into the three main groups as follows (Fig. 30.4).

1. *Fibrous materials*, i.e. with fibres of one component distributed in another (the base), Fig. 30.4*a*.

[1] Written together with B. A. Klypin.

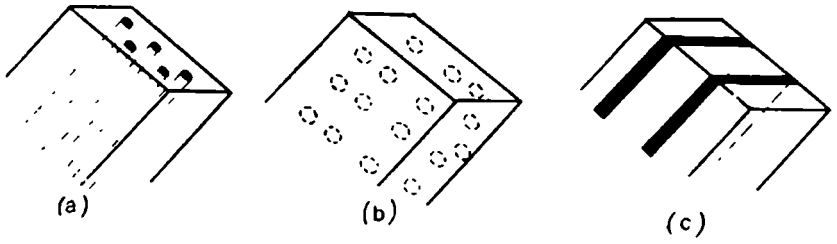

Fig. 30.4. Composite materials (schematic)

2. *Disperse materials* which consist of a matrix material and particles of one or more components distributed as a mechanical mixture in the base (Fig. 30.4*b*).

3. *Laminated materials*, i.e. those consisting of two or more layers of unlike components, Fig. 30.4*c*. Bimetals, which have been discussed in the previous section, can be related to this group.

Composite materials in each of the groups can be classified differently: by the type of component materials, their size, shape, orientation, and also by the method of manufacture or the purpose of application. For instance, fibrous materials can be divided according to the type of their matrix into metallic, polymeric and ceramic; by the type of fibres, into those reinforced with wire, glass, boride, carbon, ceramic and other fibres or with thread-like crystals; by the size of fibres, into materials with continuous or discrete (short) fibres; by fibre orientation, with fibres oriented in one, two or more directions.

Metallic composite materials are represented by the two main classes: precipitation-hardened materials (Fig. 30.4*b*) and fibre-reinforced metals (Fig. 30.4*a*).

Precipitation-hardened composite materials (metals and alloys) contain uniformly distributed particles of oxides or other compounds (nitrides, carbides, borides, etc.) which remain stable at temperatures near the melting point of the matrix. In stressing, the matrix bears the main load, whereas disperse particles act as obstacles for the motion of dislocations. Precipitation-hardened composite materials differ from common age-hardening alloys in the nature of strengthening and method of manufacture.

The degree of precipitation hardening depends on the size, shape and shear modulus of particles, the average distance between them, and the nature of bond between the particles and the matrix. The optimal properties are usually obtained at a concentration of particles within 2-15 per cent (by volume), their size of 0.01-0.1 μm, and a spacing of 0.1-1 μm between particles. Materials of this type are usually made by powder metallurgy techniques, i.e. by preparing fine powders or powder mixtures and their pressing, sintering and plastic working.

Figure 30.5 shows the effect of temperature on the long-term strength of precipitation-hardened nickel and a high-strength nickel alloy. The main advantage of precipitation-hardened materials is an appreciably higher working temperature compared to common alloys on the same base. These materials can be characterized by structural stability and a high heat resistance at temperatures up to $0.9T_{m.p.}$ ($T_{m.p}$ is the melting point of the matrix). They are however inferior to common alloys as regards the strength at low and moderate temperatures (up to $0.7T_{m.p.}$), plasticity, deformability and weldability, and are also substantially more expensive. These drawbacks limit the possibilities of application of precipitation-hardened materials. At present, precipitation-hardened materials on the basis of aluminium, nickel and tungsten are manufactured industrially.

Precipitation-hardened aluminium containing 6-23 per cent of aluminium oxide Al_2O_3, also called SAP (*sintered aluminium powder*), excels appreciably the deformable and casting aluminium alloys in the strength at temperatures above 300°C (Fig. 30.6). The compositions and mechanical properties of Soviet-made SAP grades are given in Table 30.1. SAP is almost equivalent to pure aluminium as regards the density and corrosion resistance.

SAP is a very promising material for aircraft engineering, ship-building, chemical engineering and nuclear engineering. It can be used as a substitute for stainless steels and titanium alloys in various structures operating at 250-500°C, which makes it possible to reduce substantially the mass of the structures.

Precipitation-hardened nickel. A number of precipitation-hardened nickel-base alloys have been developed to allow the use of nickel alloys at temperatures

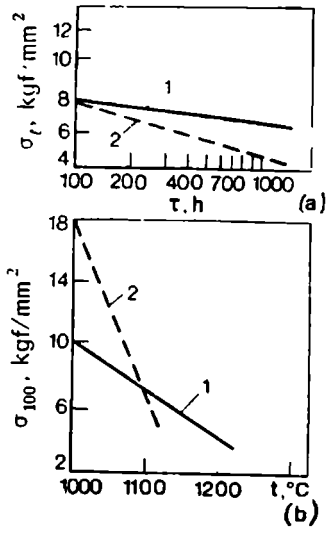

Fig. 30.5. Heat-resisting properties of (*1*) ВДУ2 alloy and (*2*) high-strength casting nickel alloy

(*a*) depending on the time of testing at 1 100°C; (*b*) depending on temperature

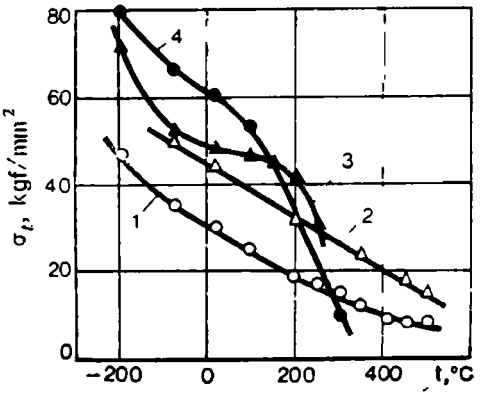

Fig. 30.6. Temperature variations of the ultimate strength of SAP and high-strength aluminium alloys

1 — SAP-1; *2* — SAP-4; *3* — Д16; *4* — В95

Table 30.1. Mechanical Properties of SAP Rods

SAP alloy Grade	Al_2O_3, % (vol.)	t_{test}, °C	σ_t, kgf/mm^2	$\sigma_{0.2}$, kgf/mm^2	δ, %	Long-term strength, kgf/mm^2	
						σ_{100}	$\sigma_{10\,000}$
SAP-1	6-9	20	28	22	10	—	—
		300	17	13	5	8.5	7
		500	6	5.5	4	4	3
SAP-2	9-13	20	34	23	7	—	—
		300	17.5	15.5	5	—	—
		500	8.5	8	2.5	—	—
SAP-3	13-18	20	42	34	4.5	—	—
		300	20	15	5.5	9.5	8
		500	11	9	3	5	4
SAP-4	18-23	20	44	—	—	—	—
		300	27	—	—	—	—
		500	15	—	—	—	—

up to 1 100-1 200°C. The highest heat resistance has been shown by a nickel alloy containing 2-3 per cent of thorium dioxide (ВДУ-1 alloy). A nickel alloy strengthened by hafnium dioxide particles (ВДУ-2 alloy) has a somewhat lower heat resistance, but is not toxic. The mechanical properties of ВДУ-2 alloy are given in Table 30.2.

Table 30.2. Mechanical Properties of ВДУ-2 Alloy

Semi-product	Temperature, °C	σ_t	$\sigma_{0.2}$	δ	ψ
		kgf/mm²		%	
Sheets	20	50-55	40-45	12-15	—
Rods		45-50	30-35	20-24	70-75
Sheets	500	26-30	20-22	5-9	—
Rods		22-25	18-20	21-24	40-50
Sheets	800	20-23	18.5-21	3-5	—
Rods		14-16	12-14	12-18	25-35
Sheets	1 000	14-16	13-14	7-8	—
Rods		9.5-10	8-8.5	8-10	20-25
Sheets	1 100	10-11	8.5-9.5	7-10	—
Rods		9.5-10	8-8.5	8-10	20-25
Sheets	1 200	7.5-8.5	6.5-7.5	5-8	—
Rods		8-8.5	7.5-7.8	7-9	15-20

As compared to the conventional heat-resisting alloys, these materials show an appreciably lower softening effect as the time and temperature of the tests are increased (within 1 000-1 300°C).

Thoriated tungsten. Tungsten containing 1-2 per cent (by volume) of ThO_2 is used as a high-emissivity material in electron devices. At temperatures up to 1 650°C, thoriated tungsten has a lower strength than certain tungsten- or molybdenum-base alloys, but at temperature above 2 200°C it is the sole material that has a higher strength than unalloyed tungsten. The mechanical properties of thoriated tungsten are given in Table 30.3.

Exceptionally high values of strength and rigidity can be obtained by reinforcing common metals with high-strength fibres. In such materials, fibres are the main load-bearing components and the matrix only transfers the external load to fibres, protects them from external actions and imparts to the composition certain physico-chemical properties, such as resistance to oxidation and corrosion, electric and thermal conductivity, etc.

Table 30.3. Mechanical Properties of Thoriated Tungsten

ThO_2 % (vol.)	σ_t, kgf/mm², at temperature, °C			σ_{100}, kgf/mm², at temperature, °C	
	1 650	1 930	2 200	1 370	1 650
0	17.5	11.4	4.4	7	3.2
1	26.0	19.6	9.8	—	—
2	20.7	18.6	12.3	16.2	7.4

The strength of composite fibrous materials depends on the following factors: the mechanical properties of the matrix and fibres; the volume concentration of fibres, their distribution and orientation; the firmness of bond at the matrix-fibre interfaces, and the thermal stability of fibres in the matrix.

The properties of composite materials at elevated temperatures may be affected by the physico-chemical interaction between the matrix and fibres, resulting in dissolution or softening of fibres and the formation of brittle interlayers at the boundaries.

Extensive research work is being carried out on developing new types of fibre-reinforced metals and alloys and testing them in experimental structures. The most promising among them seem to be aluminium alloys reinforced with fibres of borides, carbon, stainless steel and beryllium; titanium alloys with fibre reinforcement of molybdenum and beryllium, and nickel alloys reinforced with fibres of tungsten, molybdenum and their alloys. Selected properties of reinforcing fibres and fibre-reinforced metals are given in Tables 30.4 and

Table 30.4. Properties of Reinforcing Fibres

Material and type of fibre	$t_{m.p.}$, °C	Density, g.cm³	σ_t, kgf mm²	E, kgf mm²	Typical diameter, μm
Glass	700-900	2.50-2.66	350-510	73-101	10
SiO_2	1 660	2.19	595	73.5	35
Al_2O_3	2 040	3.15	210	175	—
ZrO_2	2 650	4.84	210	350	—
Carbon (graphite)	3 650	1.50	245	210	5
Boron	2 300	2.63	280	385	102
SiC	2 690	4.09	210	490	76
Tungsten	3 410	19.4	406	413	13
Molybdenum	2 620	10.2	224	364	25
Steel (wire)	1 400	7.74	420	203	13
Beryllium	1 280	1.83	129	245	27
Whiskers:					
Al_2O_3	2 040	3.96	2 100	434	3-10
SiC	2 690	3.18	2 100	490	1-3
Si_3Ni_4	1 900	3.18	1 400	385	—
Graphite	3 650	1.66	1 990	714	—

Table 30.5. Strength of Selected Metals Reinforced by Unidirectional Continuous Fibres

Composition		B	t_{test}, °C	σ_{av}, kgf/mm²	σ_{av}/γ, km
matrix	fibres				
Aluminium	SiO_2	0.47	20	91.0	37.5
		0.47	500	30	12.4
	Al_2O_3	0.35	20	112.7	35.5
	Steel	0.25	20	121.1	30.2
	Boron	0.12	20	36.5	13.4
	Boron	0.53	20	79	29.2
Copper	Tungsten	0.77	20	178.5	10
Titanium (Ti + 6% Al + 4% V)	Molybdenum	0.40	760	59	11.5
Nickel (ЖС6-К)	Tungsten	0.45-0.50	1 100	53.8	4
			1 200	38.5	2.9

Note. B = volume fraction of fibres; σ_{av} = average ultimate strength; γ = = density.

30.5. These materials are most promising for application in elements operating under the conditions of uniaxial tension, such as turbine and compressor blades. The maximum working temperatures of these materials are close to the melting

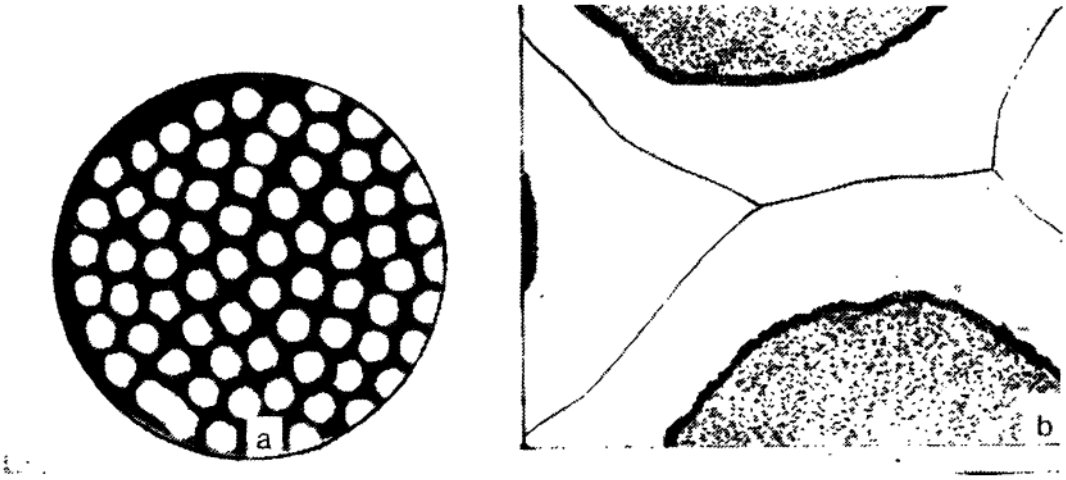

Fig. 30.7. Macro- (*a*) and microstructure (*b*) of tungsten-fibre reinforced Nichrome

point of the matrix. Figure 30.6 shows as an example the effect of temperature on the strength of glass- and quartz-fibre reinforced aluminium compared to the strength of precipitation-hardened aluminium and an aluminium alloy. Figure 30.7 illustrates the macro- and microstructure of a rod made of a tungsten-fibre reinforced Nichrome alloy (50% of fibre concentration).

Owing to the high strength (especially the strength-to-density ratio) and the possibility of obtaining the desired combination of properties by proper selection of the matrix and fibres, and by varying the concentration and orientation of the fibres, fibre-reinforced metals will undoubtedly find a wide industrial application, though certain serious difficulties associated with the technology of manufacture of these materials and the methods of design and calculation of parts made of them must be overcome.

30.3. AMORPHOUS METAL (METALLIC GLASS) [1]

The general theory of solidification of liquids states that, at a very deep undercooling of a melt, the number of crystallization nuclei and the rate of crystal growth may be equal to zero (see Fig. 2.6) and that a melt may thicken into a glass-like state without crystallization. For a long time practical attempts to obtain such a state in metals were a failure and many researchers were sceptical about the possibility of obtaining glass-like metals. However, the solidification of metals and alloys obeys the general laws of the theory of solidification and suggests that this state is principally possible in metals. In recent years, amorphous metals have been obtained experimentally.

This has been favoured, in the first place, by the progress in quick freezing techniques. In the method applied for the purpose, a falling droplet of liquid metal is flattened between two deep-frozen copper plates. The best results are obtained by 'shooting' a droplet along the radius of a fast-rotating coller disc on which the droplet is spread into a thin film. The rate of cooling attains 10^5-10^6°C/s.

The first successful experiments have been carried out with the alloys of noble metals (Au, Pd) and 17-25 per cent (at.) of a semiconductor element (Si, Ge). Radiograms and electronograms of amorphous metals are of the type similar to those of their melts (there are no diffraction spots nor rings). The electric resistivity of an amorphous metal is close to that of the molten metal. A proof of the amorphous state is that the metal liberates much heat (which should be regarded as the evolution of the latent heat of crystallization) on being heated to a definite temperature, usually near 300°C. The metal undergoes crystallization at that temperature, i.e. a change from amorphous to crystalline state; the time pattern of this transformation is in full agreement with the laws of crystallization. The process can be interrupted by cooling and the structure of the metal will then consist of fine crystals distributed in a glass-like phase.

[1] Written together with A. A. Zhukov.

The first structural amorphous component obtained in commercial metals was a ternary phosphide eutectic which forms at a temperature near 950°C. In 1974, phosphorus-free cast iron with 3.8% C was obtained in amorphous state.

Attempts to obtain pure metals or alloys of several metals have been unsuccessful as yet. A metal can be made amorphous by the existing methods of fast cooling if only it contains a certain quantity of a metalloid or semiconductor.

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